ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION: THE POLYMERIZATION OF CARBONYL-CONTAINING DIENES

By

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Nothing in the world can take the place of persistence. Talent will not; nothing is more common than unsuccessful men with talent. Genius will not; unrewarded genius is almost a proverb. Education alone will not; the world is full of educated derelicts. Persistence and determination alone are omnipotent.

Calvin Coolidge

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Abstract of Dissertation Presented to the Graduate School
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ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION: THE POLYMERIZATION OF CARBONYL-CONTAINING DIENES

By

Jasson Todd Patton

DECEMBER 1992

Chairman: Dr. K. B. Wagener
Major Department: Chemistry

Various monomers containing the carbonyl group have been investigated in order to study the acyclic diene metathesis (ADMET) polymerization of highly polar functionalities. The carbonyl containing dienes possessed the ester, carbonate, and ketone groups. These monomers were also used to study structure control in the repeat unit and structure reactivity relationships of the monomer.

New unsaturated polyester, polycarbonate, and polyketone structures have been synthesized via the acyclic diene metathesis (ADMET) polymerization. The polymerizations were performed using the catalyst $\mathrm{Mo(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}}i\mathrm{\text{-}Pr_2)[OCCH_3(CF_3)_2]_2}$ (R = Me, Ph) which was found to be much faster in the metathesis of some terminal olefins than its tungsten counterpart.

No metathesis activity is observed for ester or carbonate containing dienes when only one methylene spacer is present between the functionality and the olefin due to a negative neighboring group effect. This negative neighboring group effect involves either the coordination of the carbonyl oxygen to the metal center or simply the polarization of the double bond such that the intermediates of the metathesis process are not favored.

Some substituted ketone containing dienes were found to undergo cyclization rather than linear polymerization to yield five, six, or seven-membered rings. The cyclizations are due to a "Thorpe-Ingold" effect forcing the reactants into a horseshoe conformation conductive to cyclization.

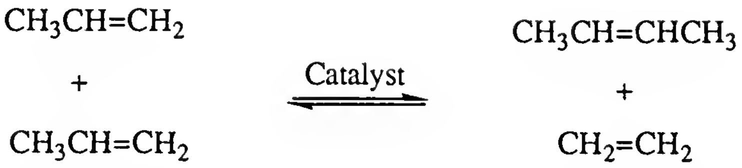
CHAPTER 1

INTRODUCTION

Successful polymer chemistry is based on predictable reactions that join one molecule to another. Two of the most challenging aspects of polymer synthesis relate to structure control in the repeat unit and to the structure reactivity relationships of the monomers themselves. Both of these challenges are dealt with in this dissertation, specifically with regard to the preparation, via acyclic diene metathesis (ADMET) polymerization, of a new class of unsaturated polymers containing the carbonyl functionality.

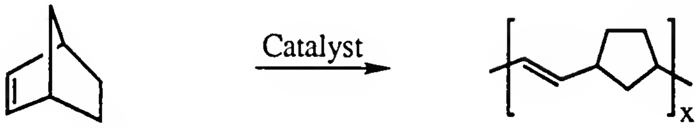
Olefin metathesis describes the interchange of carbon atoms between a pair of double bonds. Metathesis can be demonstrated with three general types of reactions (Figure 1.1).[1] The term "olefin metathesis" was first coined by Calderon in 1967, and the first publications describing olefin metathesis reactions involved the ring opening polymerization of norbornene (Figure 1.1.2) and the exchange reaction of propene (Figure 1.1.1).[2,3] These publications were preceded by patent disclosures as early as 1957.[1,4] Early work in the field of olefin metathesis has led to more than 35 years of scientific research in the field as well as several very important

1.1.1) Exchange Reactions



$$\begin{matrix} CH_3CH{=}CH_2 \\ + \\ CH_3CH{=}CH_2 \end{matrix} \xrightleftharpoons{\text{Catalyst}} \begin{matrix} CH_3CH{=}CHCH_3 \\ + \\ CH_2{=}CH_2 \end{matrix}$$

1.1.2) Polymerization Reactions



1.1.3) Degradation Reactions

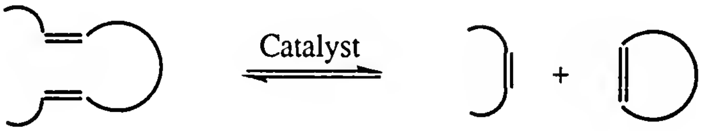


Figure 1.1. Three types of olefin metathesis reactions.

commercial applications. Particularly important has been the work in determining the mechanism responsible for metathesis chemistry, research which is described in the following section.

Mechanism of the Olefin Metathesis Reaction

A pairwise mechanism was originally proposed as the pathway for olefin metathesis where the chemistry was thought to occur when two double bonds approached one another in the vicinity of a transition metal catalyst site (Figure 1.2.1).[1] The transition metal orbitals were believed to overlap with the olefin double bonds to allow exchange to occur via a weakly held cyclobutane type complex. While this mechanism predicted most products successfully, it was eventually abandoned in favor of the metal carbene mechanism proposed in 1970 by Chauvin (Figure 1.2.2).[5,6] The evidence supporting the latter mechanism is vast, with perhaps the strongest support coming from the study of cross-metathesis reactions as well as the reactions of isolable metal carbenes with olefins which allowed the direct spectroscopic observation of metal carbene complexes and metallacyclobutane complexes.[1]

The evidence in favor of the metal carbene mechanism from cross-metathesis reactions arises from the analysis of the statistical ratio of the of the reaction products possible from the two mechanisms. A metathesis reaction between cyclopentene and the unsymmetrical olefin, pent-2-ene, would lead initially to the formation of 2,7-decadiene by the pairwise mechanism. However, when the reaction was performed using $WOCl_4/Bu_4Sn$ or $WOCl_4/$

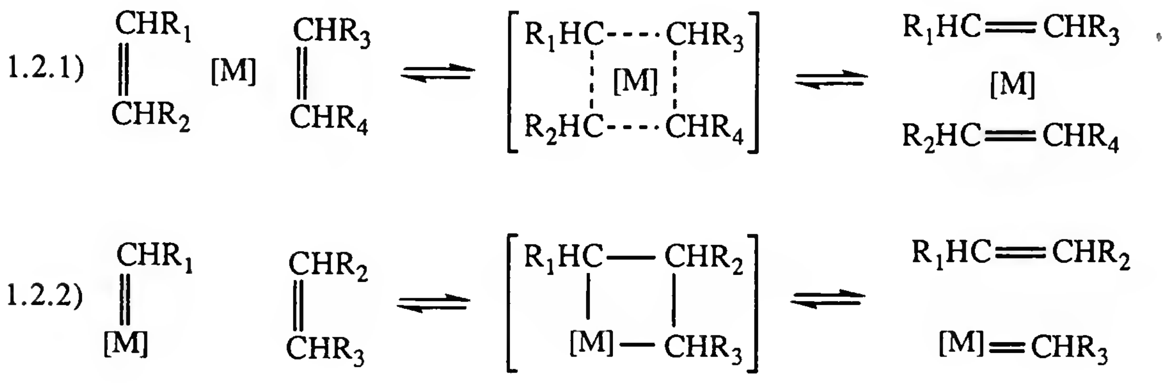


Figure 1.2. Proposed mechanisms for olefin metathesis where [M] represents a transition metal catalyst.

Et_2AlCl as catalysts the products found were 2,7-nonadiene, 2,7-decadiene, and 3,8-undecadiene in the statistical ratio of 1:2:1 (Figure 1.3).[5] It was this observation which led to the proposal of the metal carbene mechanism. The formation of the ratio of products is explained in terms of the sequence of reactions shown in Figure 1.4. Similar results were obtained with cyclooctene, cycloocta-1,5-diene, cyclododeca-1,5,9-triene in place of cyclopentene.

These results alone, however, did not disprove the pairwise mechanism. If one of the olefinic bonds remains attached to the catalyst site after the reaction, until another acyclic olefin becomes

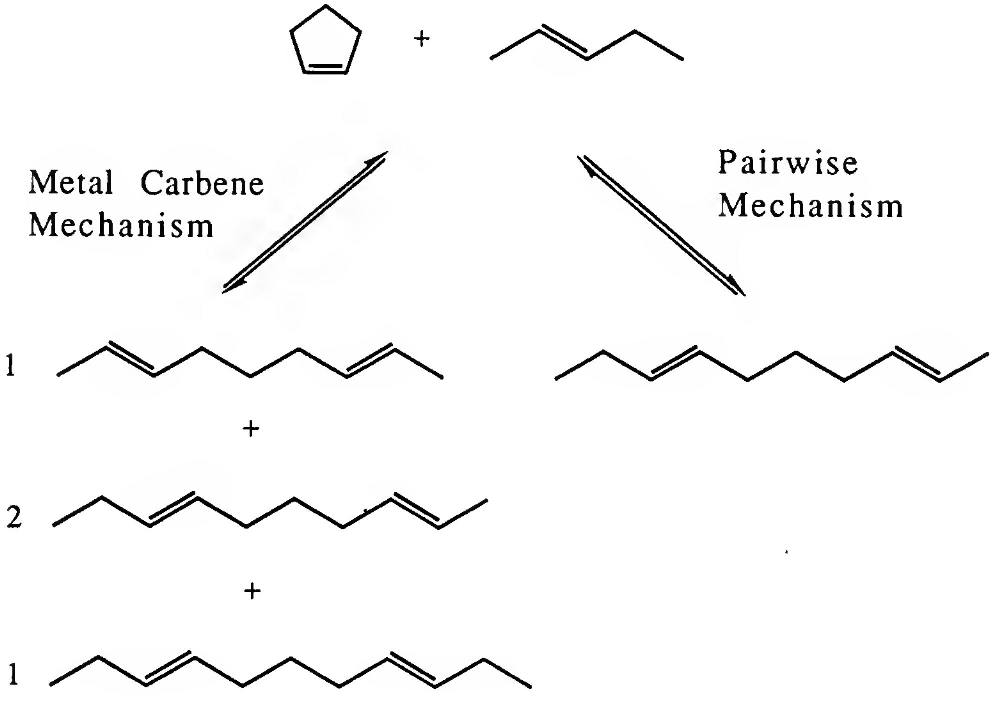


Figure 1.3. Expected products and ratios of the metal carbene and the pairwise mechanisms.

attached at the vacant site, the formation of 2,7-nonadiene and 3,8-undecadiene can be accounted for as a result of a very rapid second reaction. This explanation was referred to as the sticky olefin mechanism.[1]

A more decisive experiment was that of a double cross metathesis reaction when cyclooctene was reacted with a mixture of but-2-ene and oct-4-ene (Figure 1.5).[7] In the case of each of the proposed mechanisms the predicted values of $(n_2/n_1)(n_2/n_3)$ are 4.0 for the metal carbene mechanism, 0.0 for the simple pairwise mechanism, and 2.7 for the sticky pairwise mechanism. The actual values obtained for $(n_2/n_1)(n_2/n_3)$ were 4.05 for cis reactants and 4.1 for trans reactants. This experiment shows that both types of pairwise mechanisms must be rejected in favor of the metal carbene mechanism.

The evidence in favor of the metal carbene mechanism from the reactions of isolable metal carbenes with olefins is vast and rapidly growing today due to the synthesis of well defined catalyst systems. The first cases of characterizing initiating and propagating metal carbene species by NMR were reported in 1980.[8,9] The first reactions involved $Me_3CCH{=}WCl_2(O)(PEt_3)_2$ activated by $AlCl_3$ which induced the metathesis of but-1-ene and of pent-1-ene. In the case of but-1-ene the species $EtCH{=}WCl_2(O)(PEt_3)_2$ and $CH_2{=}WCl_2(O)(PEt_3)_2$ are both detectable by ^1H NMR. The carbene protons appear at 12.03 ppm for the reactant, 12.1 ppm for $EtCH{=}WCl_2(O)(PEt_3)_2$, and 12.34 and 11.47 ppm for $CH_2{=}WCl_2(O)(PEt_3)_2$. The nonequivelence of the protons in $CH_2{=}WCl_2(O)(PEt_3)_2$ and the fact that there is only one chemical

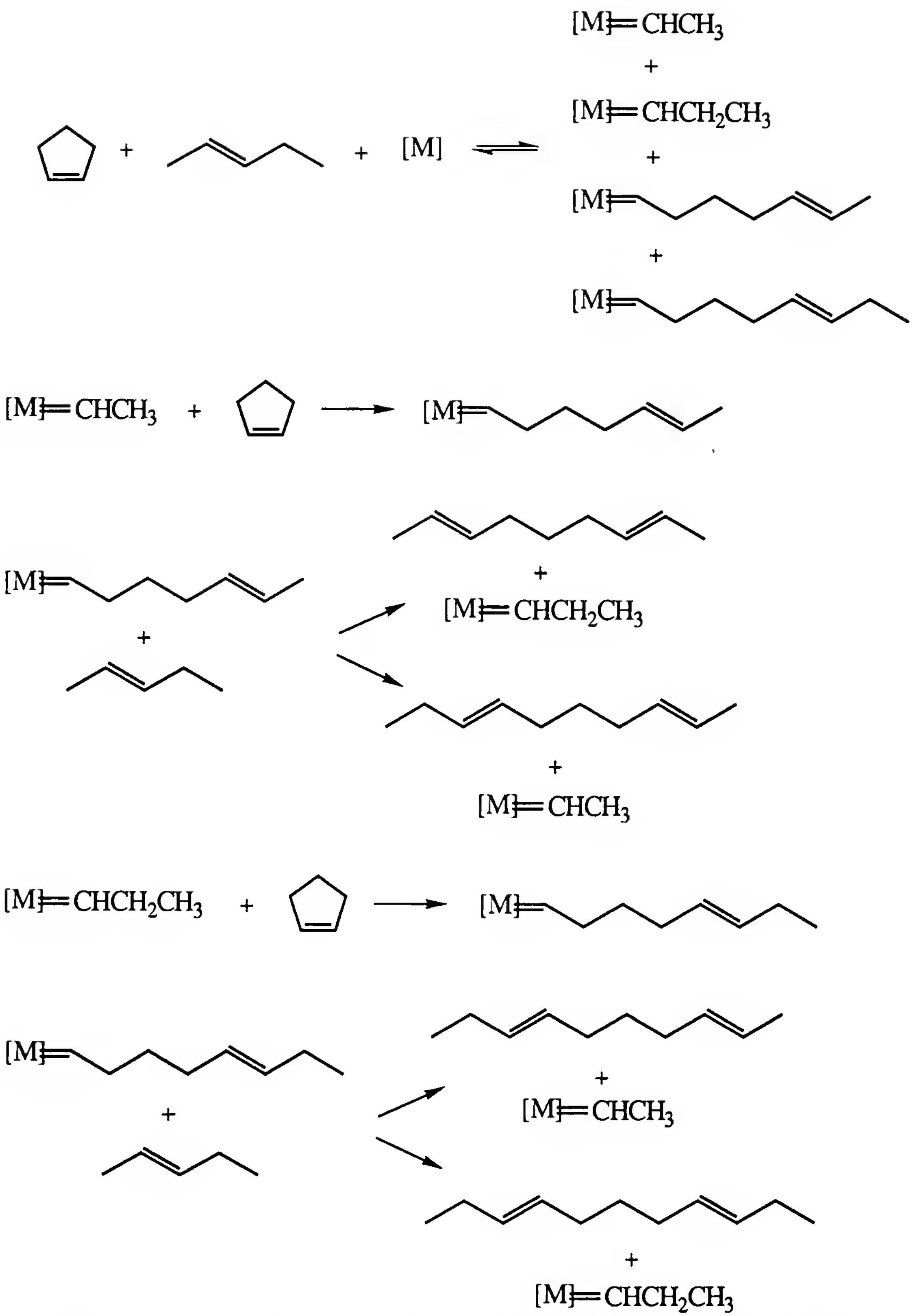

[M]=CHCH3
+
[M]=CHCH2CH3
+
[M]
[M]=
+
[M]=
[M]=CHCH3
+
[M]=
[M]=
+
+
[M]=CHCH2CH3
+
[M]=CHCH3
[M]=CHCH2CH3
+
[M]=
[M]=
+
+
[M]=CHCH3
+
[M]=CHCH2CH3

Figure 1.4. Reaction sequence demonstrating the formation of the product ratios where [W] is a tungsten based metathesis catalyst.

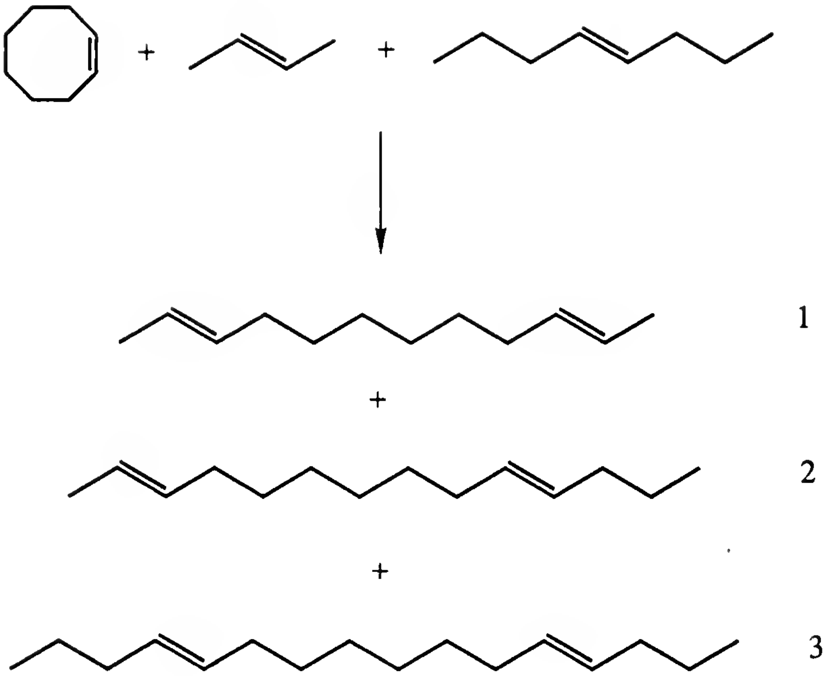


Figure 1.5. Metathesis reaction demonstrating that both types of pairwise mechanisms must be rejected.

shift for $EtCH=WCl_2(O)(PEt_3)_2$ demonstrates that the carbene ligand has a fixed orientation with respect to the other ligands. For the reaction with pent-2-ene the propagating carbenes, $EtCH=WCl_2(O)(PEt_3)_2$ and $MeCH=WCl_2(O)(PEt_3)_2$ are both present in comparable amounts.[9] There are many examples since these experiments in which metal carbenes and metallacycles have been isolated and extensively characterized.

Classical Catalyst Systems used in Metathesis Polymerizations

Classical catalyst systems that have been extensively studied in the olefin metathesis reaction commonly employ multiple components, which are generally based on a transition metal complex and an accompanying co-catalyst that serves as a Lewis acid to activate the transition metal catalyst. In these classical systems, it is assumed that the acting catalyst is a metal carbene; however, the nature and the origin of these metal carbenes often are not known or understood. In addition, classical metal catalyzed polymerizations are often plagued by a variety of side reactions which are not easily monitored.

Many classical catalyst systems have been studied in an attempt to elucidate the formation and nature of the active species. The $WCl_6/LiCH_2SiMe_3$ catalyst system produces Me_3SiCl suggesting that $CH_2{=}WCl_4$ is the reactive species (Figure 1.6).[10] The WCl_6/Me_4Sn and WCl_6/Me_2Zn systems both generate CH_4 making it reasonable to postulate the formation of $CH_2{=}WCl_4$ in these cases as well; however, the true nature of these catalyst systems have yet to be proven.[11,12]

The first evidence that the transition metal exists in a very high oxidation state appeared when isolable complexes of the type $W(CH\text{-}t\text{-}Bu)(O)L_2Cl_2$ (L=trialkylphosphine) were found to promote a metathesis reaction in the presence of $AlCl_3$ to yield $W(CHR')(O)L_2Cl_2$ complexes.[8] Soon after, complexes of the type $W(CH\text{-}t\text{-}Bu)(OR)_2X_2$, were shown to be extraordinarily active toward olefin metathesis in the presence of AlX_3. The four coordinate cationic species of the form, $[W(CHR')(OR)_yX_{3-y}]^+$, are believed to be the most active of components of these systems.[8,13-17]

$$WCl_6 + LiCH_2SiMe_3 \longrightarrow Me_3SiCH_2WCl_5 \longrightarrow \underset{\text{observed}}{Me_3SiCl} + \underset{\text{postulated}}{CH_2{=}WCl_4}$$

Figure 1.6. Typical classical metathesis catalyst in which the active catalyst system is poorly defined.

The most important catalyst systems are based on the fourteen transition elements shown in Table 1.1.[1] Over the last three decades vast numbers of catalyst systems have been explored for their proficiency in the olefin metathesis reaction. The most successful catalyst systems, by far, have been based on the transition metals, tungsten and molybdenum. The primary limitation of these catalysts is their inability to be prepared systematically and their reactivity controlled by rational means. This limitation has been a particularly frustrating problem in the search for catalyst systems compatible with functional groups and eventually led to the synthesis of well defined catalyst systems.

Table 1.1. Transition elements commonly used as catalysts.

Group IVA	Group VA	Group VIA	Group VIIA	Group VIII
Ti	V	Cr		
Zr	Nb	Mo		Ru Rh
Hf	Ta	W	Re	Os Ir

Ring Opening Metathesis Polymerization (ROMP) and the Synthesis of Well-Defined Catalyst Systems

In recent years research in the area of ROMP has led to the development of very active and well-defined metathesis catalyst systems. The belief was that a highly active four coordinate, neutral olefin metathesis catalyst would alleviate the potential for complications that can occur in the presence of highly active cationic catalyst systems, and the first of these well defined catalyst systems was developed by Schrock (Figure 1.7).[13,18] These catalyst systems are well defined in that the initial metal complex is already a metal carbene which is not the case with most classical olefin metathesis catalysts. These well defined systems have led to a far greater understanding of the olefin metathesis reaction than was previously attainable since it allows substituted and unsubstituted metallacyclobutanes to be isolated and characterized.[13,18] These well defined catalyst systems have also allowed various mechanistic as well as kinetic studies to be performed which were not feasible for classical catalysts.[13]

The tungsten based metal complex, $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OR)_2$, synthesized by Schrock, was the first Lewis acid-free catalyst system to be studied.[18] In addition to the factors mentioned above, this complex showed that catalysts can be prepared systematically and their reactivity controlled by rational means. An example can be seen in the case where the complex $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OR)_2$ was prepared and the metathesis activity controlled through the choice of the alkoxide ligand.[13] While several model studies were done, the one most

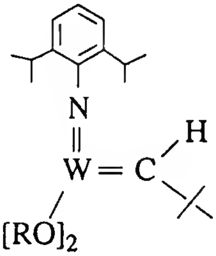


Figure 1.7. Lewis acid-free catalyst developed for ROMP.

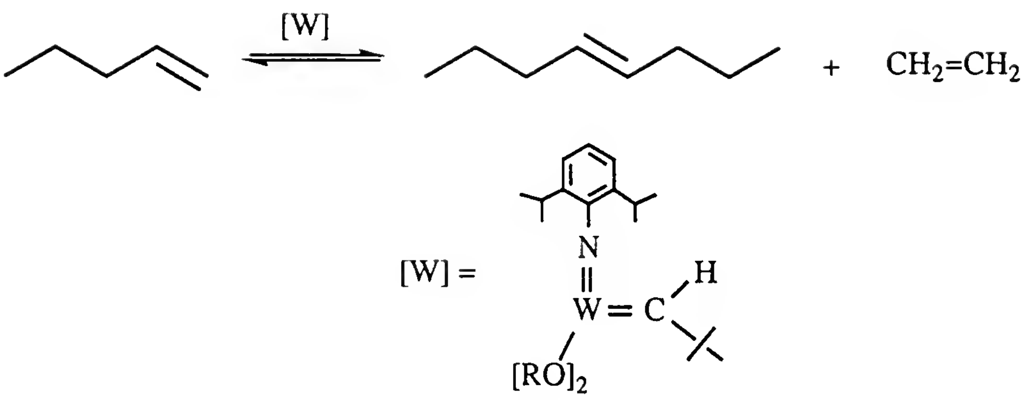


Figure 1.8. Dependence of metathesis rates on alkoxide.

relevant to this research was the metathesis of 1-pentene to give neohexene. In the case where $R=C(CH)_3$, the reaction proceeded slowly reaching 70% conversion after eight hours. In neither case are more than a few turnovers to ethylene and 4-octenes observed in several hours (Figure 1.8). When $R=C(CH_3)_2CF_3$ was employed as the alkoxide, the reaction was faster but as in the previous case only low conversions to ethylene and 4-octenes were observed. However, in the case where $R=CCH_3(CF_3)_2$, the reaction was very rapid and reached 75% conversion after only ten minutes to give $W(CHPr)(NAr)[OCCH_3(CF_3)_2]_2$, the beta-substitited tungstacycle $W(CH_2CHPrCH_2)(NAr)[OCCH_3(CF_3)_2]_2$, and the unsubstituted metallacycle $W(CH_2CH_2CH_2)(NAr)[OCCH_3(CF_3)_2]_2$. Experiments have shown that the reason for the differences in reactivity lies in the fact that the stability of the intermediate metallacycles when $R=CCH_3(CF_3)_2$ is far greater than in the other two cases where the alkoxide ligands are less electron withdrawing. In the final case where $R=C(CF_3)_2(CF_2CF_2CF_3)$ again only low conversions were observed despite immediate catalyst reaction.

Two possible reasons for this last observation are that the beta-propyl metallacycle may be relatively stable toward loss of olefin (Figure 1.9.1), or, for steric reasons it may be the only metallacycle that forms (Figure 1.9.2). This study of alkoxide ligands showed that catalyst structures can be systematically produced and the reactivity controlled by the choice of the alkoxide ligand. The final results of this study clearly show that the most active olefin metathesis catalyst of this series has $R=CCH_3(CF_3)_2$ as the alkoxide.[13]

The nature of the metal center also affects catalyst reactivity, and the purpose of investigating catalyst systems based on various metal centers has been to find active systems compatible with functional groups.[19,20] For example, when $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCCH_3(CF_3)_2)_2$ was reacted with ethyl acetate or cis-methyl-9-octadecenoate the catalyst lifetime was limited by a Wittig type reaction (Figure 1.10). This chemistry has been observed in catalyst systems based on tantalum, titanium, and zirconium as well as tungsten.[21] The molybdenum analogue of catalyst W(CH-t-

1.9.1)

1.9.2)

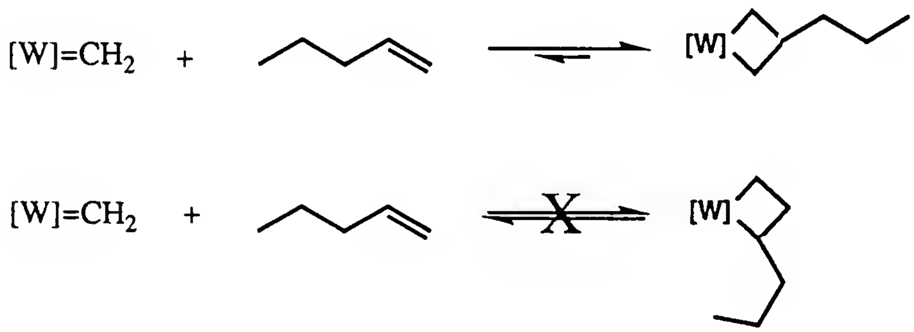
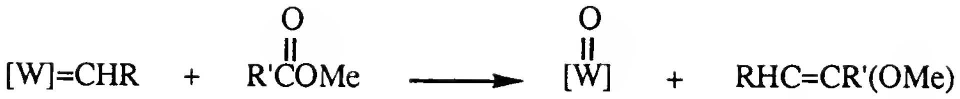


Figure 1.9. Possible reactions of tungstacyclobutane complexes when $[W]=W(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OCCH_3(CF_3)_2)_2$ and $R=C(CF_3)_2(CF_2CF_2CF_3)$.



$$[W]{=}CHR + R'\overset{O}{\overset{\|}{C}}OMe \longrightarrow \overset{O}{\overset{\|}{[W]}} + RHC{=}CR'(OMe)$$

Figure 1.10. Wittig-type chemistry of a tungsten-based catalyst where R=t-butyl and $[W]=W(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OR)_2$.

$Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OR)_2$ was synthesized for the reason that the metal-carbon bond in $Mo(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OR)_2$ is not as strongly polarized as in the tungsten analogue.[19] This lack of polarization means that the molybdenum based catalyst might not react as readily with highly polar functionalities such as the ester group.

The experimental evidence that the molybdenum based catalyst is more tolerant to the carbonyl functionality than the tungsten based catalyst is considerable.[19-27] $Mo(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OC(CH)_3)_2$ did not react with ethyl acetate or with N, N-dimethylformamide even over a period of several days meaning that the catalyst was stable to some highly polar functionalities.[20] $Mo(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OR)_2$ was found to react rapidly in a Wittig fashion with benzaldehyde when $R=C(CH)_3$ and $R=CCH_3(CF_3)_2$. The same catalysts also reacted rapidly with acetone; however, the products could not be identified.

Similar results were obtained when an actual polymerization was carried out using the different metal based catalysts. $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OC(CH)_3)_2$ was found to polymerize endo, endo-5,6-dicarbomethoxynorbornene, but the catalyst was rapidly

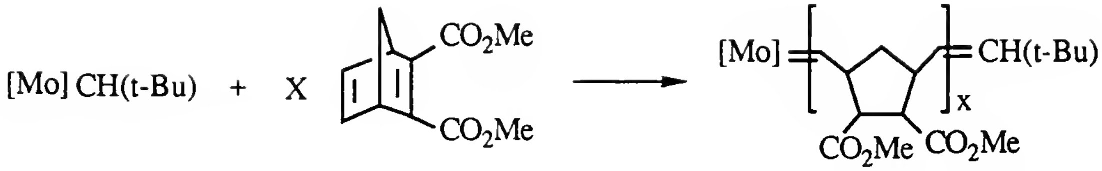


Figure 1.11. Living polymerization of endo, endo-5, 6-dicarbomethoxynorbornene.

destroyed and the molecular weight therefore cannot be controlled. However, when endo, endo-5,6-dicarbomethoxynorbornene is reacted with Mo(CH-t-Bu)(N-2,6-C_6H_3-*i*-Pr_2)($OC(CH)_3)_2$, a polymer is produced that has a low polydispersity, characteristic of a living polymerization catalyst system (Figure 1.11).[19] This initiated a vast research effort to polymerize many functionalized norbornenes in addition to the ester functionality.[22-24,26-27]

Acyclic Diene Metathesis (ADMET) Polymerization

A second approach to olefin metathesis polymerization via acyclic diene metathesis (ADMET) chemistry was conceived many years ago but was not realized until 1987.[28] An ADMET polymerization involves an olefin exchange reaction (Figure 1.1.1) where the monomer is a diene (Figure 1.12). The ADMET polymerization is a step condensation polymerization driven by the removal of the condensate, and since the polymerization involves

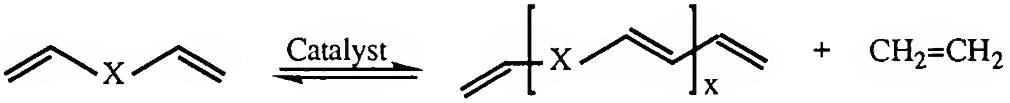


Figure 1.12. Acyclic Diene Metathesis (ADMET) polymerization.

an equilibrium process, the polymerization is reversible.[29] Early experiments attempting to polymerize 1,9-decadiene and 1,5-hexadiene to polyoctenomer and polybutadiene, respectively, failed.[28] These experiments employed classical catalyst systems such as $WCl_6/EtAlCl_2$, and while metathesis products were observed, a large percentage of intractable material resulted.

The intractable material was shown to be the result of a competing vinyl addition reaction resulting from the formation of a cation due to the presence of the Lewis-acid. The vinyl addition reaction was shown to be the side reaction most clearly in a model study using styrene (Figure 1.13). In the case of styrene, if metathesis occurs then the resulting product is stilbene; however,

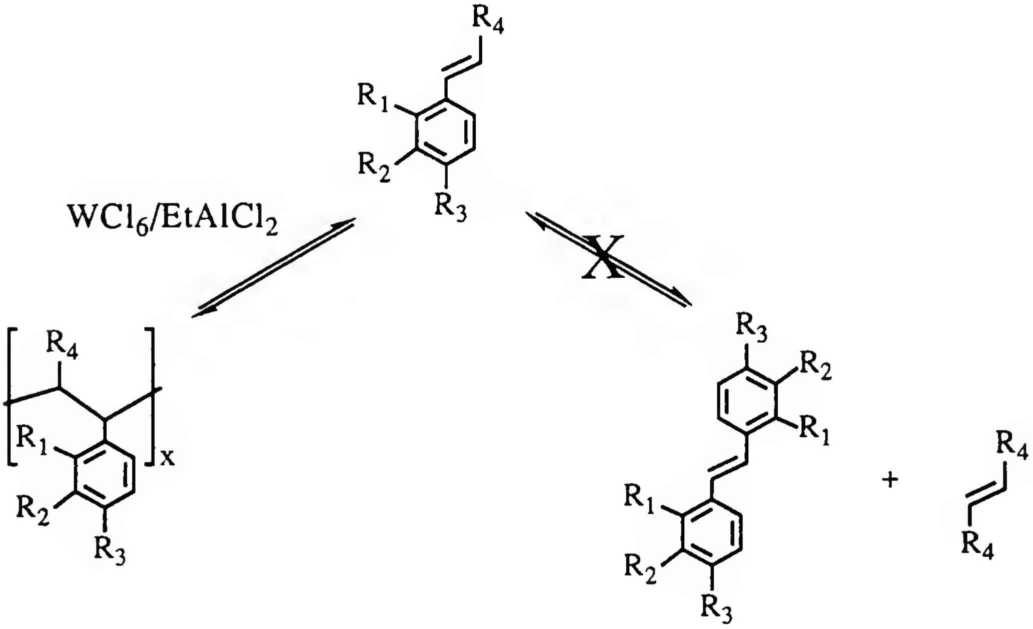


Figure 1.13. ADMET model study with styrene and a classical catalyst system (R_1, R_2, and R_3 are either F, H, Br, or CH_3 or combinations thereof. R_4 is either H or CH_3.).

if vinyl addition occurs then the product is polystyrene. As illustrated in Figure 1.13, the only observed product is polystyrene.[28]

The development of the Lewis acid-free catalyst systems (Figure 1.7) discussed previously offered the possibility of using a catalyst system where the cationic center is not formed in the activation of the catalyst.[18] Without the formation of the cationic center the vinyl addition reaction should not be initiated and the only product observed should be stilbene if any product forms at all. This was, in fact, observed to be the case (Figure 1.14). This result initiated the investigation of ADMET polymerization as a viable route for the synthesis of high molecular weight unsaturated polymers.[30-34]

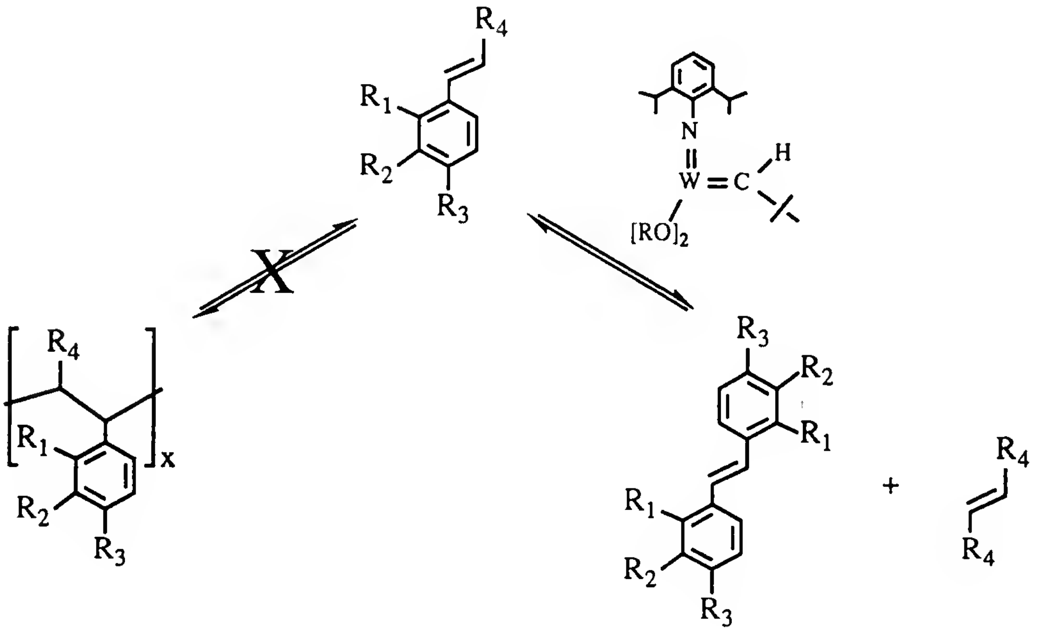


Figure 1.14. ADMET model study with styrene and a Lewis acid-free catalyst system (R_1, R_2, and R_3 are either F, H, Br, or CH_3 or combinations thereof. R_4 is either H or CH_3.).

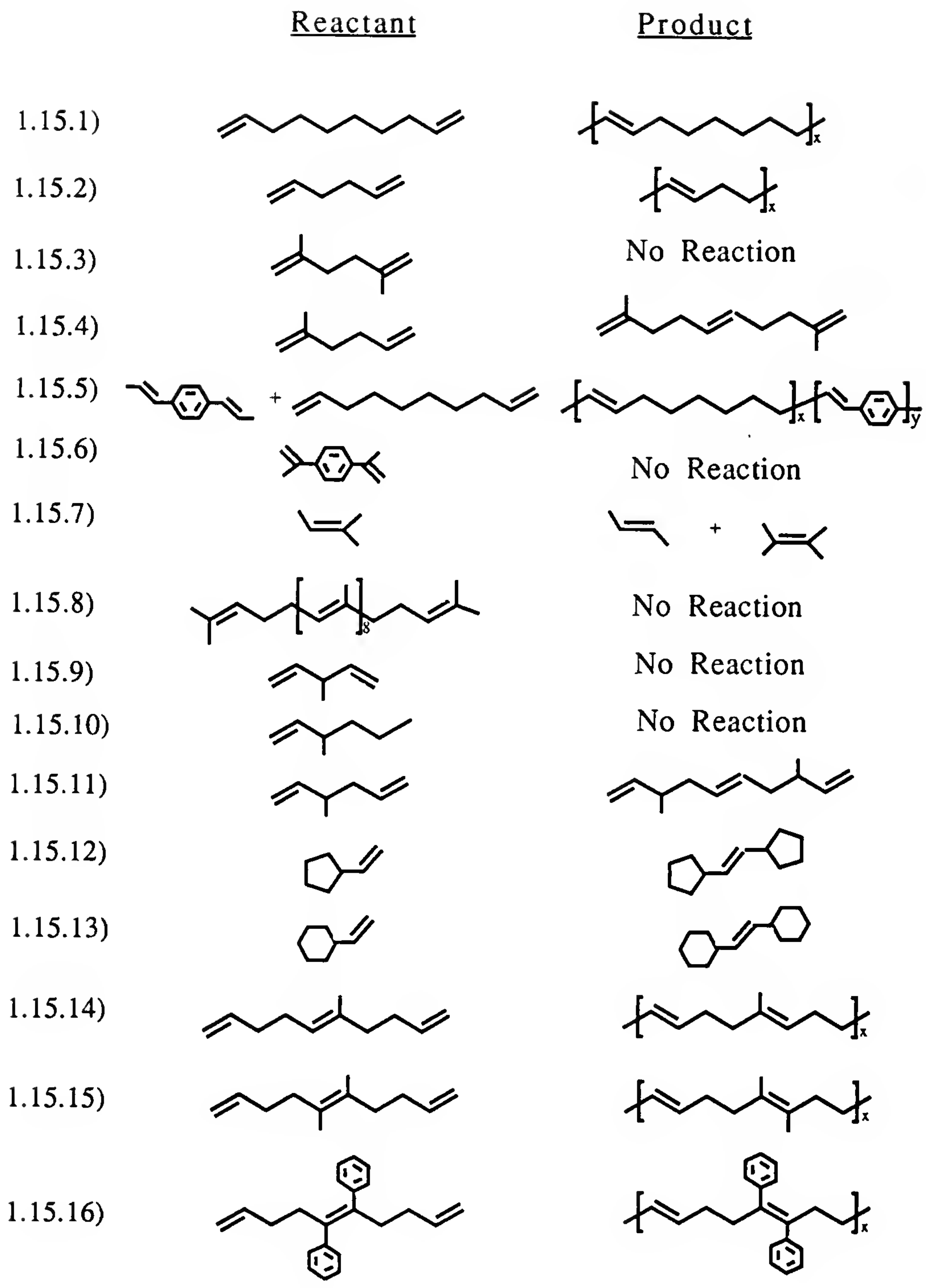

Reactant
Product
1.15.1)
x
1.15.2)
x
1.15.3)
No Reaction
1.15.4)
1.15.5)
+
x
y
1.15.6)
No Reaction
1.15.7)
+
1.15.8)
8
No Reaction
1.15.9)
No Reaction
1.15.10)
No Reaction
1.15.11)
1.15.12)
1.15.13)
1.15.14)
x
1.15.15)
x
1.15.16)
x

Figure 1.15. ADMET polymerizations and model studies involving hydrocarbon reactants.

The first ADMET polymerization carried out produced polyoctenomer from 1,9-decadiene (Figure 1.15.1); the polymer was perfectly linear and 90% trans in its stereochemistry. These characteristics were found to be the general case for ADMET polymerizations. This polymerization was followed by the polymerization of 1,5-hexadiene to poly-1,4-butadiene (Figure 1.15.2). Copolymerizations were then carried out using 1,5-hexadiene and 1,9-decadiene forming perfectly random, linear poly(butadiene-co-octenomer) copolymers.[35] The successful polymerization of the perfectly linear acyclic dienes led to a hydrocarbon monomer structure reactivity study (Figure 1.15.3-1.15.16).[36] Copolymerizations were also carried out between 1,9-decadiene and 1,4-dipropylenebenzene (Figure 1.15.5).[37] All of the reactions involving the ADMET reaction of simple alkyl olefins are shown in Figure 1.15 for completeness.

The proposed mechanism for ADMET polymerization is similar to that of ROMP since the catalytic cycle involves the formation and decomposition of various metallacycles. It differs, however, from that of ROMP since in the course of the reaction the active catalyst actually breaks free from the polymer chain (Figure 1.16).[34] While the proposed mechanism is speculative in nature, it is rational since intermediates such as those shown in Figure 1.16 have all been observed in similar systems. The polymerization cannot be considered living since the reaction has been shown to follow the Caruther's relationship for non-living step condensation polymers.[38]

The experiments discussed above clearly show that unhindered hydrocarbon monomers can be polymerized successfully. It was

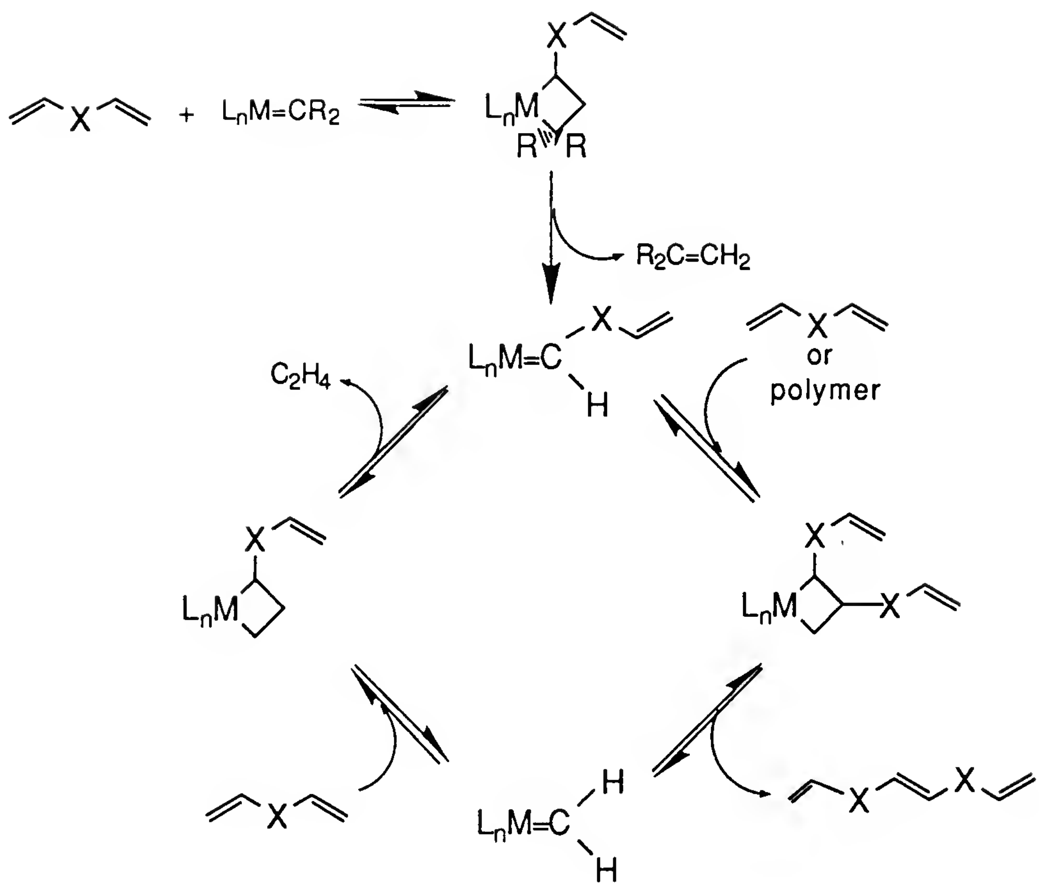

X
$L_nM{=}CR_2$
L_nM
R
R
$R_2C{=}CH_2$
$L_nM{=}C$
H
C_2H_4
or
polymer
L_nM
L_nM
X
X
$L_nM{=}C$
H
H

Figure 1.16. Proposed mechanism for the ADMET polymerization of 1,9-decadiene.

1991, however, before the ADMET polymerization of olefins containing heteroatoms was successfully demonstrated. The first of these polar olefins to be successfully polymerized were those containing the ether functionality (Figure 1.17).[39,40] These polymerizations performed by Brzezinska demonstrated the ability

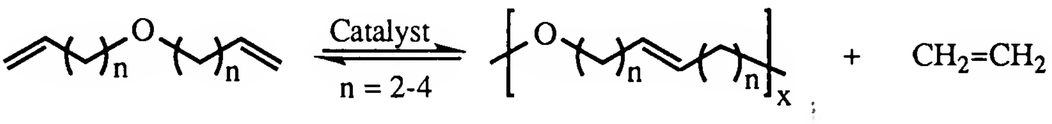

O
n
n
Catalyst
n = 2-4
O
n
n
x
+
$CH_2{=}CH_2$

Figure 1.17. ADMET polymerization of ether containing olefins.

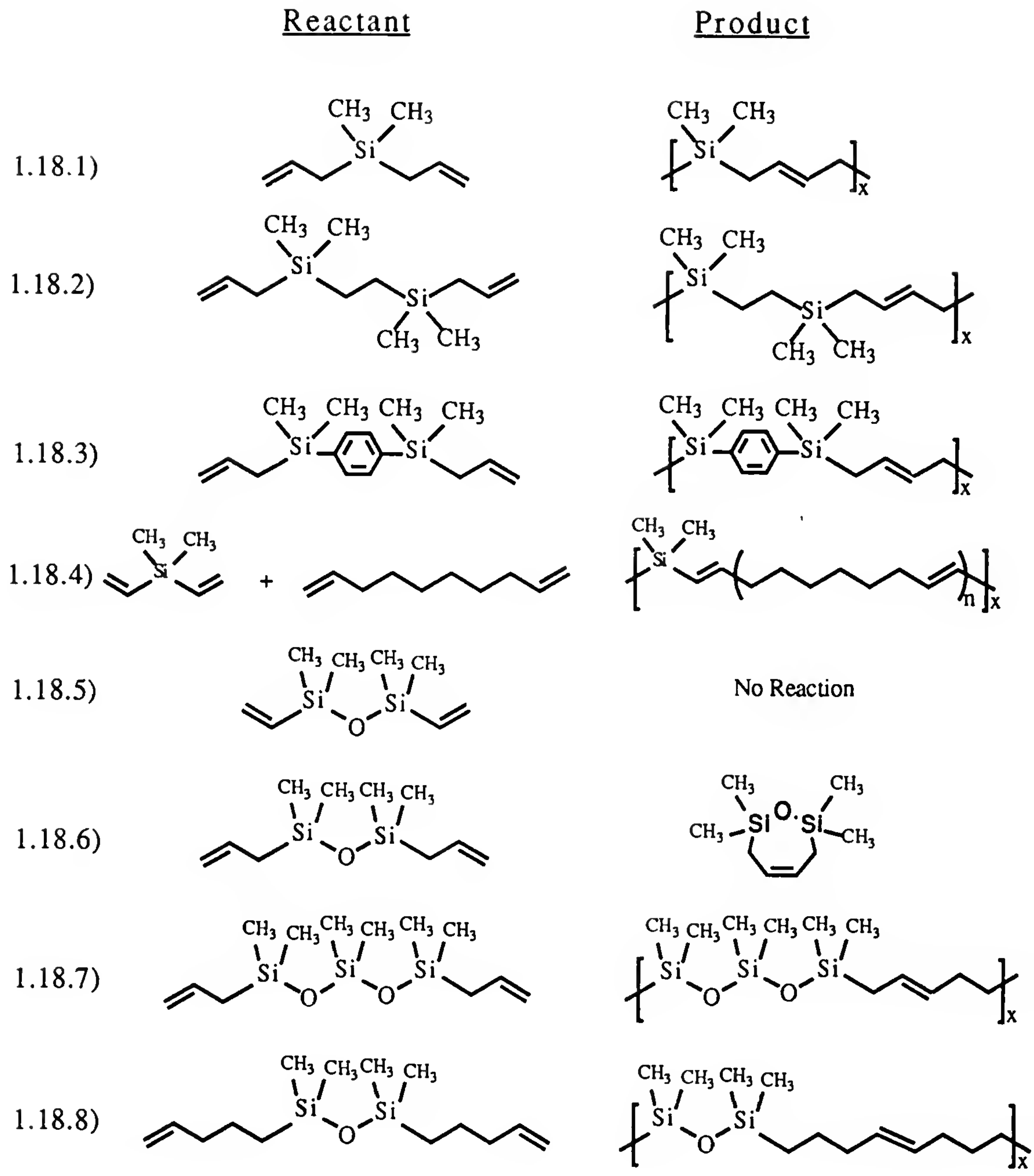
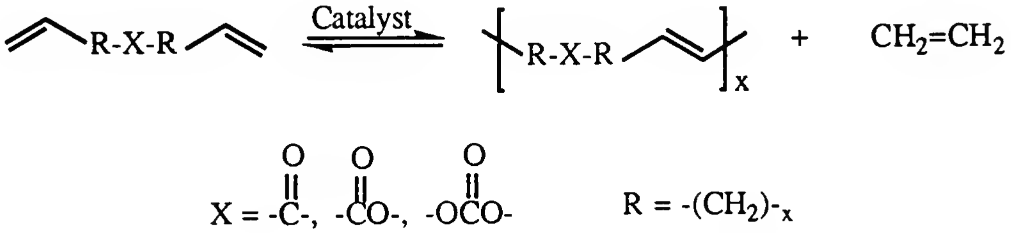

Reactant
Product
1.18.1)
1.18.2)
1.18.3)
1.18.4)
1.18.5)
No Reaction
1.18.6)
1.18.7)
1.18.8)

Figure 1.18. ADMET synthesis of poly[carbo(dimethyl)silanes] and poly(carbosiloxanes).

to polymerize monomers with polar functionalities, monomers which were previously believed to coordinate to the unsaturated metal center and therefore block any reactivity. This series of polymers was also the first reported example of unsaturated polyethers.

Soon after the ether group was shown to be tolerant toward the metathesis reaction, the silane and siloxane functionalities were introduced by Smith as a polymerizable functionalities (Figure 1.18).[41-43] Figure 1.18.1-1.18.4 demonstrates the ability to synthesize polycarbosilanes, while Figure 1.18.5-1.18.8 demonstrates the ability to synthesis unsaturated polysiloxanes. Again, all reactions are shown in this figure for completeness.

Establishing that monomers other than simple alkyl olefins can be successfully polymerized demonstrated that unsaturated polymers with highly polar functionalities might be synthesized. The polymerization of monomers containing the highly polar carbonyl group forms the basis of this dissertation (Figure 1.19). Polymers containing the ester, carbonate, and ketone containing functionalities are described in the following chapters, where structure/reactivity relationships are delineated in each case. The chemistry is unprecedented and has led to completely new polymer structures.



$X = -\overset{O}{\overset{\|}{C}}-,\ -\overset{O}{\overset{\|}{C}}O-,\ -O\overset{O}{\overset{\|}{C}}O-$ $\qquad R = -(CH_2)-_x$

Figure 1.19. ADMET polymerization of carbonyl containing monomers.

CHAPTER 2

ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION: THE SYNTHESIS OF UNSATURATED POLYESTERS

Various monomers containing the carbonyl group have been investigated in order to study the ADMET polymerization of highly polar functionalities. The first carbonyl containing functionality studied was the ester group where these ester containing dienes were condensed to yield unsaturated polyesters. Ketone and the carbonate functionalities are presented in subsequent chapters.

Conventional methods of preparing unsaturated polyesters involve the polycondensation reaction at elevated temperature between glycols and dibasic acids, esters, or anhydrides (Figure 2.1).[38,44] The useful range of number average molecular weights for these polymers is generally moderate (15,000 to 20,000), allowing for easy processibility via molding or coating. Curing of the olefin present in the repeat units is then performed via thermal

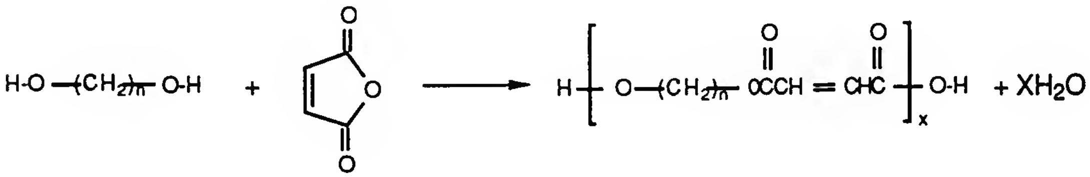
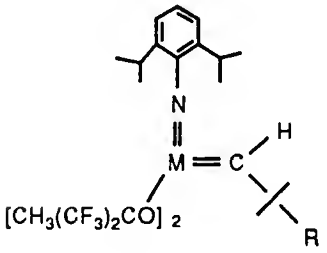


Figure 2.1. Conventional synthesis of unsaturated polyesters.

or irradiation methods. These conventional methods can result in a significant loss of unsaturation and branching during the polyesterification step. Thus, ADMET polymerization may offer a better route to unsaturated polyesters.

The metathesis of carbonyl containing compounds has received attention in the past.[1] Until the development of Lewis acid free metathesis catalyst systems, however, the metathesis of unsaturated compounds containing the carbonyl functionality had been unsuccessful due to the rapid poisoning of the catalyst system. Only low conversions were observed, and thus, highly reactive classical homogeneous metathesis catalyst systems such as WCl_6-$SnMe_4$ and $WOCl_4$-$SnMe_4$ have seen only limited success in the metathesis of unsaturated esters. Heterogeneous catalyst systems based on Re_2O_7/Al_2O_3-$SnMe_4$ also have been used in the attempted metathesis of unsaturated esters; however, as in the case for previous homogeneous catalyst systems, conversions are less than the necessary >99% required for successful step polymerization chemistry.[1,45]



Catalyst	M	R
1a	Mo	Ph
1b	Mo	CH_3
2a	W	Ph
2b	W	CH_3

Figure 2.2. Schrock's olefin metathesis catalyst.

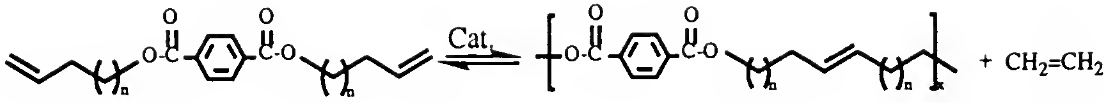


Figure 2.3. Aromatic unsaturated polyesters synthesised via the ADMET polymerization.

The molybdenum analog of Schrock's catalyst (Figure 2.2) has been described to be more tolerant of the carbonyl functionality as demonstrated in its application in the ring opening metathesis polymerization of functionalized norbornenes.[13,18-23] This chapter reports the first successful acyclic diene metathesis (ADMET) polymerization of an ester-containing monomer using this molybdenum based catalyst and demonstrates the successful polymerization of monomers containing a high degree of polar functionality, leading to unsaturated polymers possessing a high degree of crystallinity (Figure 2.3). Simple alkyl monomers were also used to define the synthesis rules of the ADMET polymerization of monomers containing the ester functionality (Figure 2.4).

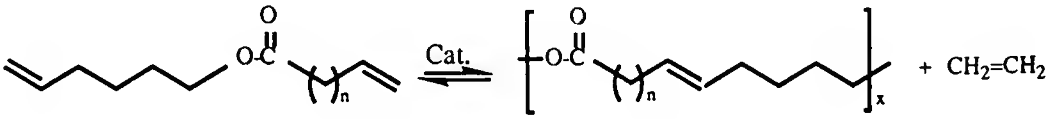


Figure 2.4. Simple unsaturated alkyl polyesters synthesized via ADMET polymerization.

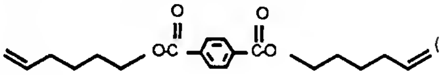
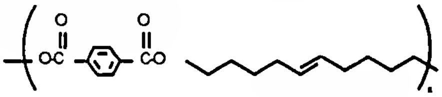
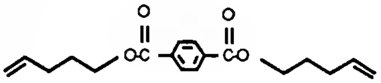
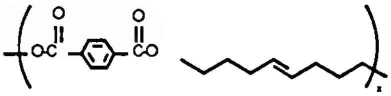
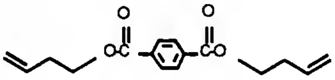
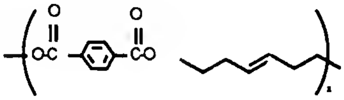
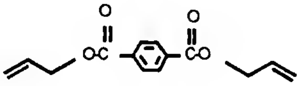
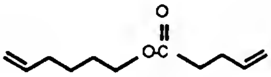
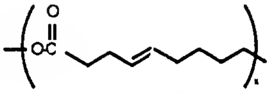
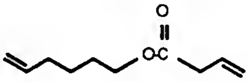
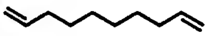
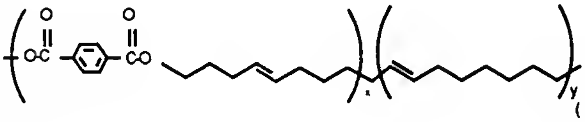
ADMET Synthesis of Unsaturated Polyesters and the Negative Neighboring Group Effect

The first example of the ADMET polymerization of esters was performed using the tungsten catalyst, 2b (Figure 2.2), and a monomer possessing eight methylene spacers between the ester functionality and the olefin.[46] While this demonstrated the viability of the ADMET polymerization of ester-containing olefins, it did not address the limitations of these polymerizations. In order to establish the synthesis rules and conditions for the polymerization of these ester monomers, a study was undertaken to determine the number of methylene spacers between the olefin and the ester group required to allow a successful ADMET polymerization.

Table 2.1 lists the unsaturated ester monomers with various numbers of methylene spacers between the ester group and the olefin used in this research. The polymerization of the linear alkyl ester, 7, demonstrates that monomers with as few as two methylene spacers from the carbonyl side of the ester polymerize successfully using the molybdenum catalyst, 1. The polymerization proceeds rapidly at room temperature and exhibits no evidence of chain transfer or branching in either the ^1H or ^{13}C NMR data as well as the optimal MWD (molecular weight distribution) of 2.0 for the polymerization. This polymerization also demonstrates the ability to rapidly synthesize high molecular weight unsaturated polyesters using the molybdenum catalyst, 1, at room temperature.

By comparison, the analogous alkyl ester, 8, in which only one methylene spacer is present, shows no evidence of metathesis polymerization at either olefin site. This result is surprising since one would have expected at some dimerization product from the side with four methylene spacers present. This shows that the

Table 2.1. Unsaturated polyesters formed via the ADMET polymerization.

Monomer	Polymer
 (3)	 (9)
 (4)	 (10)
 (5)	 (11)
 (6)	No Metathesis
 (7)	 (12)
 (8)	No Metathesis
(4) + 	 (13)

ester functionality with one methylene spacer is not inert, but reacts quickly with the catalyst destroying its catalytic activity. When Mo catalyst 1a is reacted with 14 at -80°C at a 1:1 ratio in an NMR experiment, a new peak in the alkylidene region was observed at 12.1 ppm. This new alkylidene peak may have been

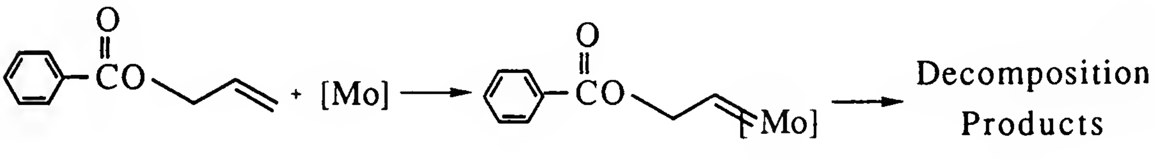


Figure 2.5. Possible reaction between 14 and catalyst 1a where [Mo] is catalyst 1a.

been the new propagating species formed upon the addition of the catalyst to the olefin; however, the new compound was very unstable and decomposed before further analysis could be performed (Figure 2.5). The experiment clearly showed that while dimerization is not taking place, the ester functionality with only one methylene spacer does react with the catalyst to yield some non-metathesizing compound.

The number of methylene spacers between the ester functionality and the olefin is a factor in these polymerizations and this observation agrees with a similar study of monomers containing the ether functionality.[39,40] The minimum number of methylene spacers between the olefin and the ester from the oxygen side is also two for successful metathesis to occur, as demonstrated with the aromatic esters 3-6. These comparisons were made under identical reaction conditions. In some classical catalyst systems, reactivity has been observed in systems with only one methylene spacer present.[45]

There are two possible reasons for this lack of reactivity when less than two methylene spacers are present and we term this phenomenon the negative neighboring group effect. First, the ester may polarize the olefin such that the successful formation and decomposition of the metallocycles in the catalytic cycle are hindered. Second, the carbonyl might coordinate with the metal center. This coordination would result in the formation of five or six member rings in the case of monomers 8 and 6, respectively, which has been proposed in similar systems(Figure 2.6).[47] The coordination of the carbonyl with the metal center of a metalla-

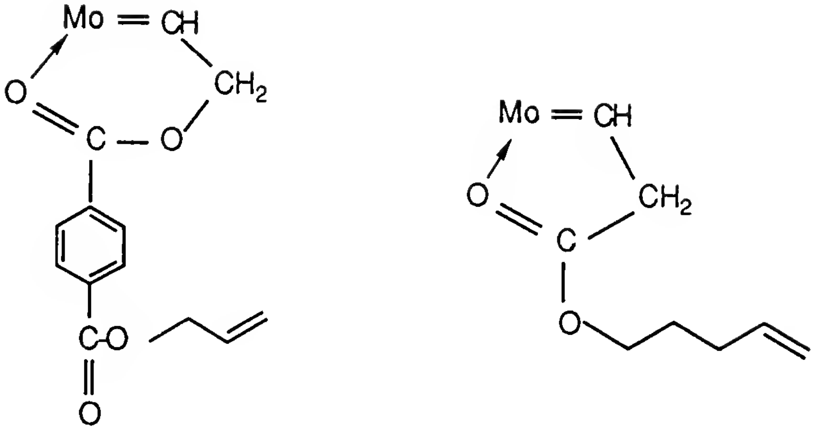


Figure 2.6. The potential coordination of monomers 8 and 6 leading to coordinatively unsaturated metal centers.

cyclobutane resulting in four member rings has been observed in similar systems.[48]

Varying the number of methylene spacers from two to four had no obvious effect on the rate of polymerization; therefore, this negative neighboring group effect appears exclusively in the one methylene spacer cases. Regardless of the reason for the negative neighboring group effect, it is clear that having less than two methylene spacers between the olefin and the ester functionality prevents polymerization.

Unsaturated Polyester Characterization and Molecular Weight Analysis

Table 2.2 compiles the reaction temperature and the molecular weight data for polymers 9-13. In all cases, the oligomers were found to be perfectly linear and pure as demonstrated by the ^{13}C NMR spectra for polymer 9 in Figure 2.6. The *trans* /*cis* ratio found in all of the polymers was similar to that observed in other ADMET systems where the polymers were found to be 80-90 % *trans*.[34] All aromatic ester polymerizations were limited by the solubility of the growing oligomer since these polymerizations ceased when the oligomers precipitated from solution at both 25 and 45°C. The polymerizations of the aromatic ester monomers 3-5 were carried out at 45°C, a temperature at which the catalyst's reactive intermediates begin to decompose. Consequently, multiple catalyst additions produced higher molecular weight oligomers; however, the active catalyst decomposed before a true equilibrium could be established, leading to non-equilibrium molecular weight dis-

Table 2.2. Molecular weight data for unsaturated polyesters.

Polymer	T (°C)	$\overline{X}_n$	$\overline{M}_n$	MWD
9	45	39	11,700	3.5
9	25	20	9,500 (9,200)	2.3
10	45	45	12,300	2.7
11	45	22	5,200	2.5
12	25	101	(18,400)	1.9
13	25	22	4,100	2.1

Refer to Table 2.1 for polymer structures. M_n in parenthesis determined by VPO; all others determined by endgroup analysis from ^{1}H NMR. The molecular weight distribution (MWD) was determined by gel permeation chromatography relative to polystyrene. .

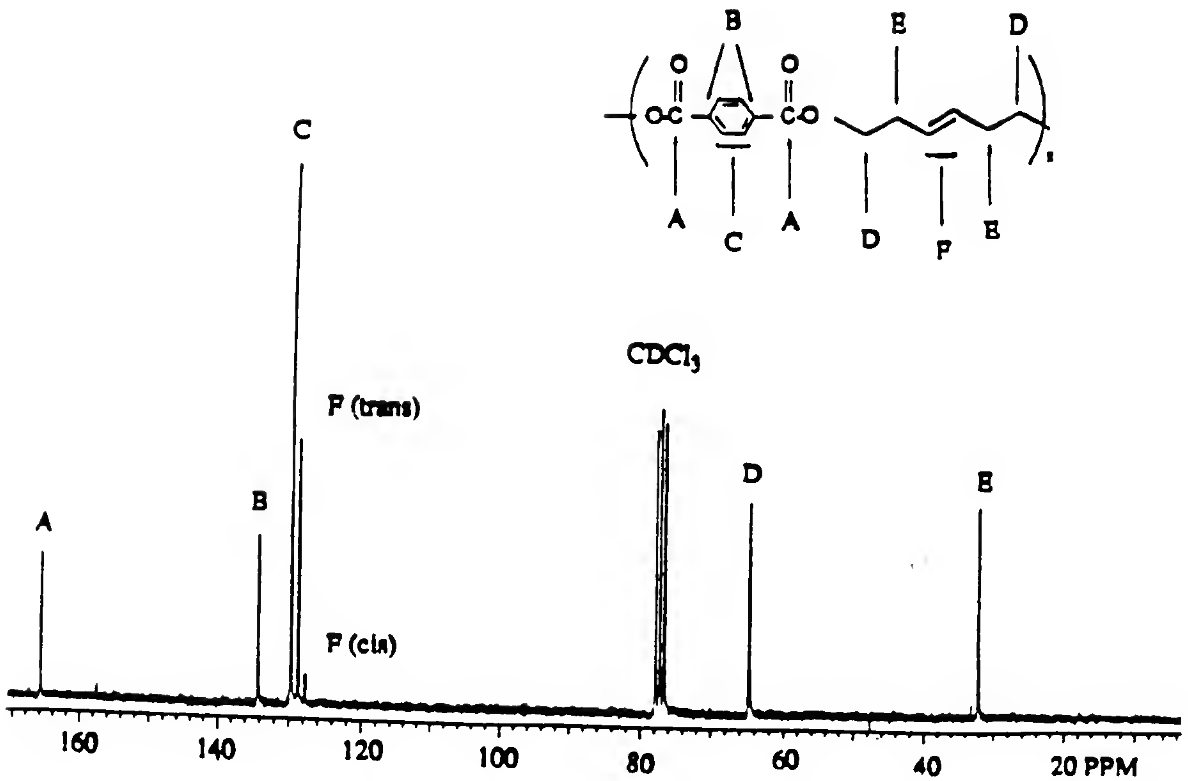


Figure 2.6. ^{13}C NMR spectra for polymer 9. The spectra was recorded using a 200 MHz instrument and CDCl$_3$ as the solvent.

tributions. The molecular weight distributions shown in Table 2.2 are reflective of a step polymerization process.

In order to demonstrate the viability of copolymerizing the aromatic esters with more flexible monomers, a copolymerization was carried out with a 1:1 mixture of 1,9 decadiene and monomer 4 and was compared with a homopolymerization of monomer 4. The homopolymerization of monomer 4 produced an average degree of polymerization of 11, limited by the solubility of the growing oligomers. An identical room temperature copolymerization resulted an average degree of polymerization of 22. The significant increase in molecular weight at room temperature is attributed to the introduction of a flexible unit. The copolymer is random in nature.

Thermal Analysis of the Unsaturated Polyesters

The thermogravimetric analysis (TGA) data in Table 2.3 shows that the unsaturated polyesters display a high degree of thermal stability. In all cases the polymers exhibited total weight loss in a single step as displayed in Figure 2.7, which is the thermogram for polymer 11 and is representative of all the curves regardless of nitrogen or air purge

The differential scanning calorimetry (DSC) results are depicted in Table 2.4. No T_g is observed for polymers 9 and 11 above -50°C even at heating rates of 20 °C/min. This observation as well as the sharpness of the transition peaks, imply a high degree of crystallinity for polymers 9 and 11. A typical DSC curve for the above mentioned polymers is displayed in Figure 2.8. Polymer 12 at slow ramp rates of 4 °C/min. shows very strong recrystallization and melting peaks with no clear T_g. At 9 °C/min, however, the crystallization peak decreases significantly, reappearing in the heating cycle overlapping with the melting peak. At this rate a clear T_g is observed. Polymers 10 and 13, which contain three methylene spacers between the olefin and the aromatic peak, exhibited very slow rates of crystallization; therefore, extrapolated thermal data were difficult to obtain. A typical thermogram of these two polymers consists of a weak melting transition upon

Table 2.3. Thermogravimetric analysis data for unsaturated polyesters.

Polymer	Onset (°C)		90 % Weight Loss (°C)	
	Air	Nitrogen	Air	Nitrogen
9	251	326	487	410
10	245	335	495	418
11	291	323	500	422
12	199	257	463	480
13	278	283	489	446

All values were obtained at a 5°C/min. heating rate.

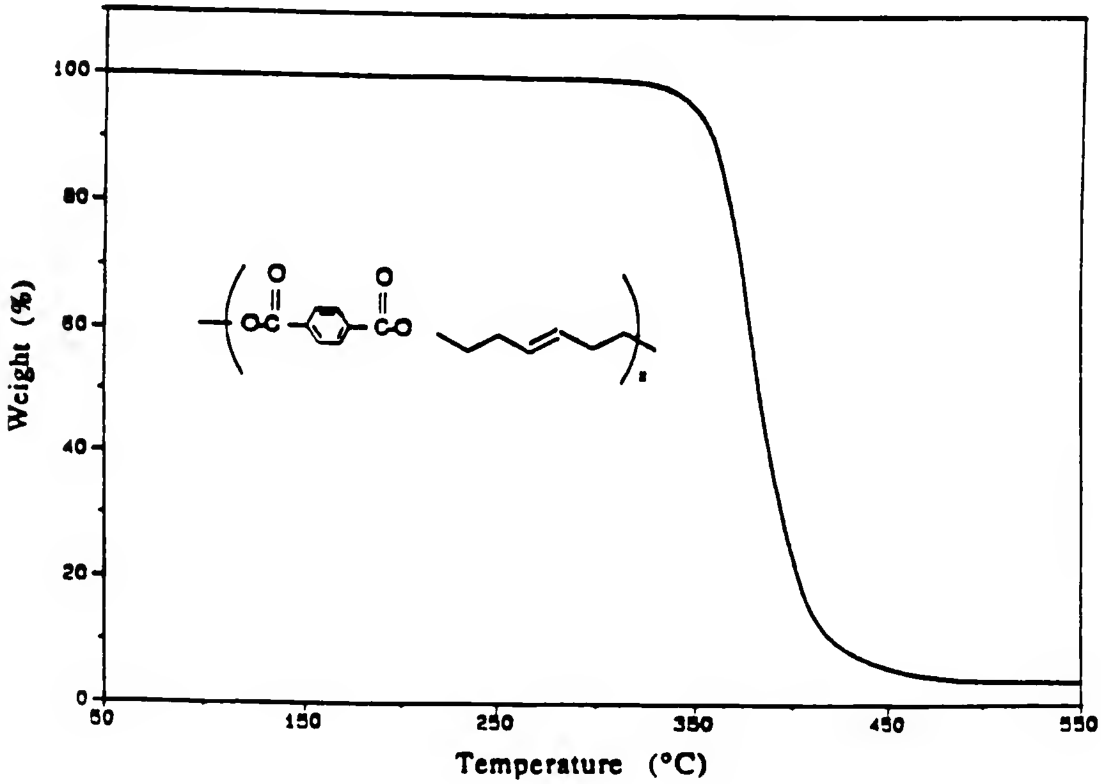


Figure 2.7. TGA thermogram for polymer 11 obtained at a 5°C/min. heating rate under a nitrogen purge.

Table 2.4. Differential scanning calorimetry data for unsaturated polyesters.

Polymer	T_m (°C)	T_c (°C)	T_g (°C)
9	$101^{a,c}$	80^{a}	--------
10	39^{b}	--------	-50^{b}
11	$162^{a,c}$	$156^{a,c}$	-------
12	-8^{c}	-27^{c}	-70^{d}
13	39^{b}	--------	-46^{b}

T_g is defined as the glass transition temperature, T_c as the temperature of crystallization, and T_m as the temperature of melting.

a: Values obtained at 20, 10, and 5°C/min. and extrapolated back to 0°C/min.
b: Values determined from a 5°C/min. cycle.
c: Values determined from a 4°C/min. cycle.
d: Values determined from a 9°C/min. cycle.
e: Bimodal with values corresponding to the inflection point of the initial peak.
f: Peak possess shoulder.

initial heating and the absence of other transitions in the remainder of the three cycles.

Kinetic Advantage of the Molybdenum Based Catalyst Versus that of Tungsten

The molybdenum catalyst, 1, offers a kinetic advantage over the tungsten catalyst, 2, in this chemistry. When 1,9-decadiene was exposed to the tungsten catalyst, 2b, in a 800:1 ratio, an olig-

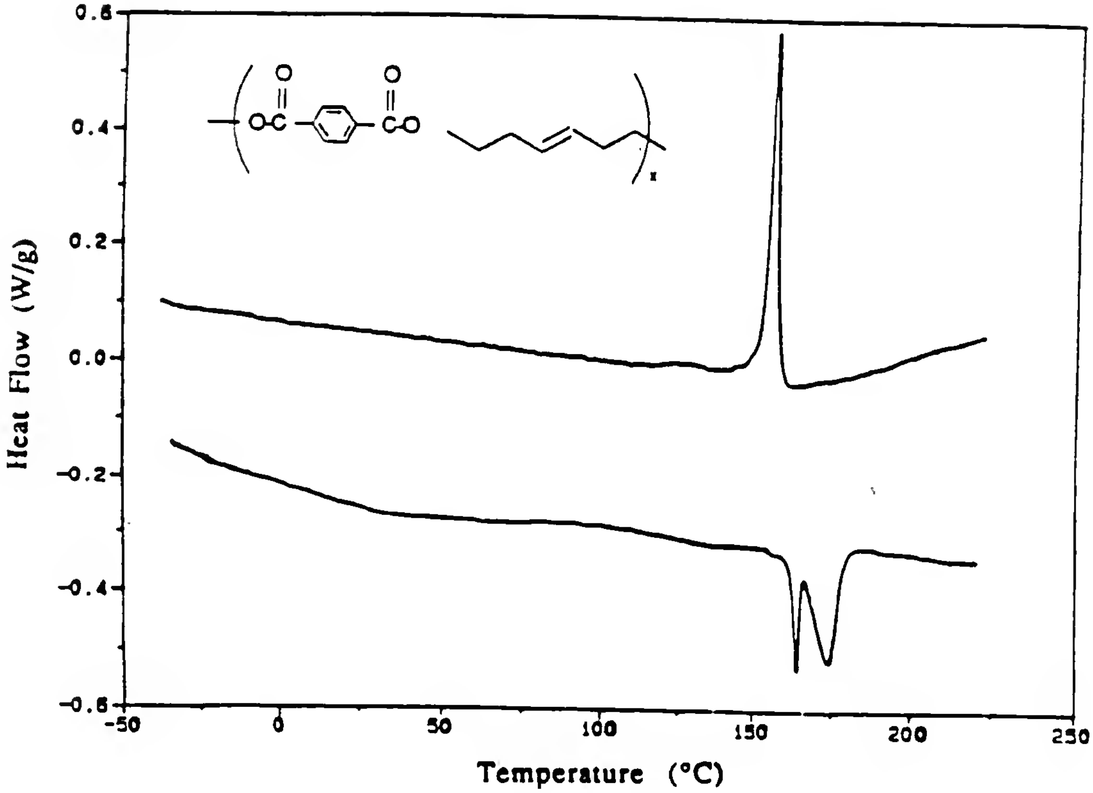
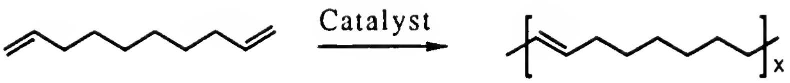


Figure 2.8. DSC thermogram for polymer 11 obtained at a heating rate of 5°C/min.

omer of $X_n = 11$ was produced within 3 hours, whereas, the molybdenum catalyst, 1b, generated this oligomer in less than 5 minutes (Figure 2.9). This dramatic increase in reaction rate is significant, and this phenomenon has been observed in similar systems.[20,49] This means that solution polymerization becomes a reality since the polymerization can proceed at a reasonable rate even when a growing polymer chain is diluted in solution. Thus, the low temperature polymerization of stiffer and less soluble polymers becomes viable.



Catalyst	$\bar{X}_n$	Time (min.)
[Mo] (1b)	11	5
[W] (2b)	11	200

Figure 2.9. Kinetic comparison between molybdenum and tungsten based catalysts performed as side by side reactions in the drybox under identical conditions at 800 moles of monomer/mole of catalyst.

Acyclic diene metathesis (ADMET) polymerization offers a viable route for the synthesis of pure unsaturated polyesters. The use of the highly active, Mo based, Lewis acid-free alkylidene catalyst provides a clean route to unsaturated polyesters with known vinyl endgroups. The polymerizability of a monomer is limited by the number of methylene spacers between the ester functionality and the olefin, a phenomenon which we term the negative neighboring group effect. The observation that molybdenum catalyst 1 successfully polymerizes acyclic dienes is significant since it is more tolerant to polar functionalities and reacts at a significantly faster rate than tungsten catalyst 2 for some terminal olefins. The successful ADMET polymerization of ester containing dienes led to the investigation of the carbonate and the ketone functionalities. The following chapters address each of these functional groups.

CHAPTER 3

ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION: THE SYNTHESIS OF UNSATURATED POLYCARBONATES

The preparation of polycarbonates is well established, as is the case with polyesters. This research targets a new synthetic route to polycarbonates. The ADMET polymerization of carbonate containing monomers further supports the evidence that monomers containing the carbonyl functionality can be polymerized.

Commercial methods of preparing polycarbonates involve either an ester interchange route carried out as a two-stage melt polymerization process or a phosgene reaction carried out in a basic solution (Figure 3.1).[1] Recently the ring opening polymerization of carbonate containing macrocycles has been reported as a route to various functionalized polycarbonates (Figure 3.2).[50-52] Poly-

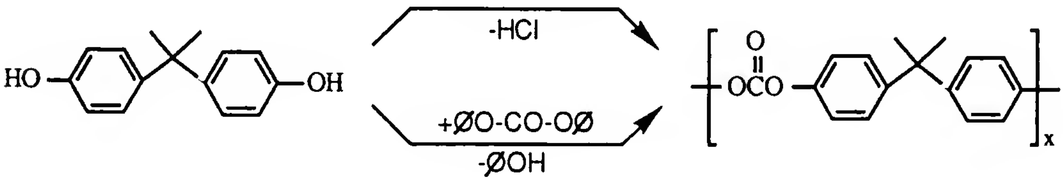


Figure 3.1. Conventional synthesis of polycarbonates.

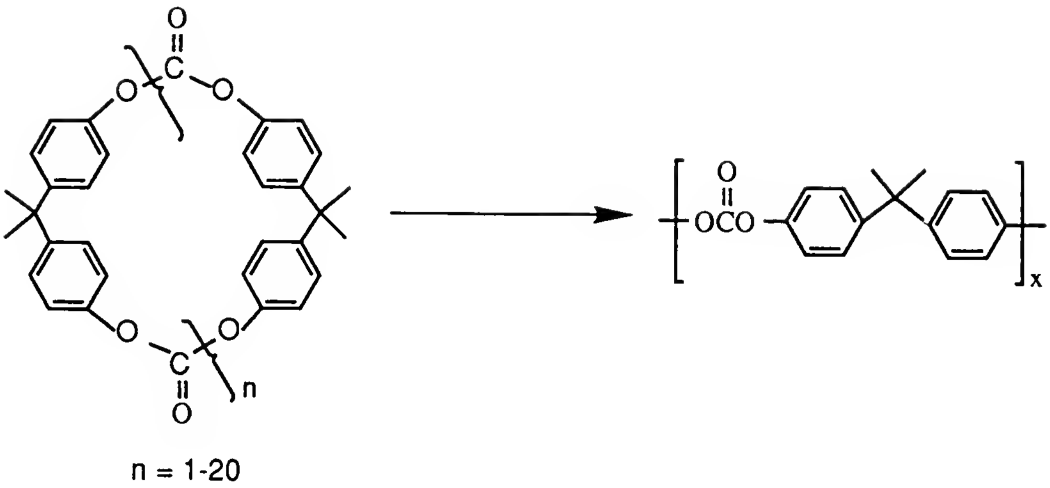


Figure 3.2. Ring opening polymerization of polycarbonates.

carbonates have found many commercial applications involving packaging, structural foam, and transparent glasses.

This chapter reports the successful ADMET polymerization of carbonate containing monomers using the molybdenum based catalyst Mo(CHCMe$_2$Ph)(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)[OCCH$_3$(CF$_3$)$_2$]$_2$, 1a, and to our knowledge, this is the first report of the metathesis of unsaturated carbonates. Simple alkyl monomers have been used to define the synthesis rules of the ADMET polymerization of monomers containing the carbonate functionality (Figure 3.3). A polymer containing the bisphenol linkage was also synthesized

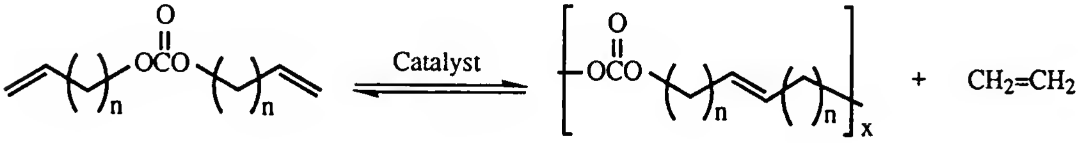


Figure 3.3. Simple unsaturated polycarbonates synthesized via the ADMET polymerization.

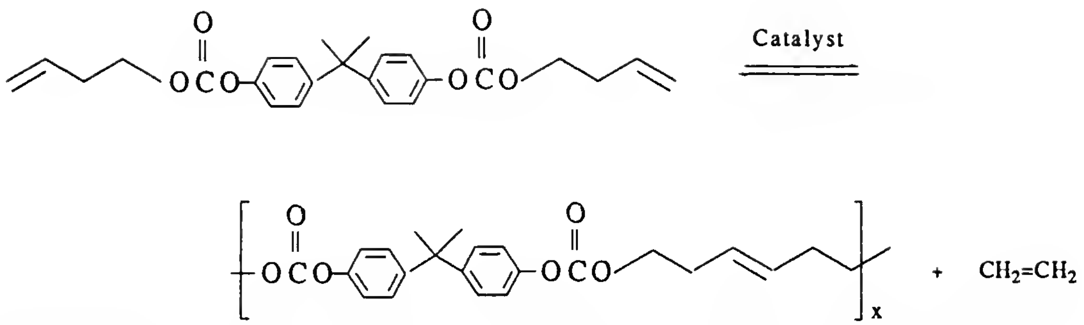


Figure 3.4. Unsaturated polycarbonate containing the bisphenol-A linkage synthesized via ADMET chemistry.

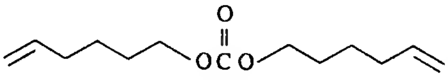
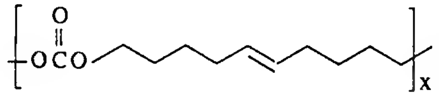
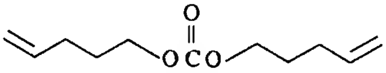
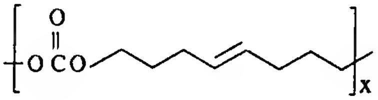
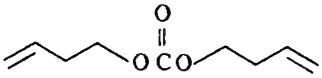
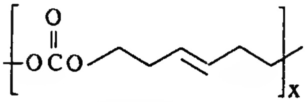
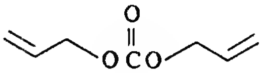
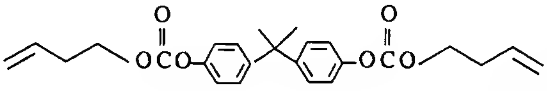
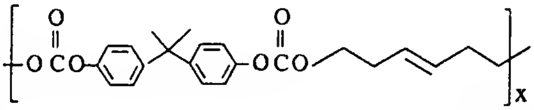
demonstrating the polymerization of a highly functionalized carbonate monomer (Figure 3.4).

ADMET Synthesis of Unsaturated Polycarbonates and the Negative Neighboring Group Effect

In order to establish the synthesis rules and conditions for the polymerization of these carbonate containing monomers, a study was undertaken to determine the number of methylene spacers required to allow a successful ADMET polymerization. A summary of the monomers studied and the polymers formed is found in Table 3.1.

Table 3.1 lists the unsaturated carbonate monomers with various numbers of methylene spacers between the carbonate group and the olefin used in this research. The polymerization of the linear alkyl carbonate, 17, demonstrates that monomers with as few as two methylene spacers between the carbonate functionality and the olefin polymerize successfully using the molybdenum catalyst. The polymerization proceeds rapidly at room temperature and exhibits no evidence of chain transfer or branching in either

Table 3.1. Unsaturated polycarbonates synthesized via ADMET polymerization.

Monomer	Polymer
 (15)	 (20)
 (16)	 (21)
 (17)	 (22)
 (18)	No Reaction
 (19)	 (23)

ality and the olefin polymerize successfully using the molybdenum catalyst. The polymerization proceeds rapidly at room temperature and exhibits no evidence of chain transfer or branching in either the ^{1}H NMR or ^{13}C NMR as well as the optimal MWD (molecular weight distribution) of 2.0. These polymerizations demonstrate the ability to rapidly synthesize high molecular weight unsaturated polycarbonates. By comparison, the alkyl carbonate, 18, in which only one methylene spacer is present, shows no evidence of metathesis.

The number of methylene spacers between the carbonate functionality and the olefin is a factor in these polymerizations. This observation agrees with similar studies of monomers containing the ether and the ester functionalities (Chapter 2).[39,40] The phenomenon of needing two methylene spacers between the functionality and the olefin has been termed the negative neighboring group effect, as described in the polyester chapter.

Unsaturated Polycarbonate Characterization and Molecular Weight Analysis

Table 3.2 compiles the molecular weight and structural data for polymers 20-23. In all cases, the oligomers were found to be perfectly linear and pure as demonstrated by the ^{13}C NMR for polymer 23 in Figure 3.5. The *trans/cis* ratio found in polymers 20-22 was similar to that observed in other ADMET polymers. This ratio for polymer 23 could not be determined since the *cis* signal overlaps with the aromatic region in the ^{13}C NMR spectra.

The gel permeation chromatography (GPC) data displayed in Figure 3.6 is typical for step condensation polymerizations except

Table 3.2. Molecular weight data for unsaturated polycarbonates.

Polymer	% Trans	$\overline{M}_n$	$\overline{X}_n$	MWD
20	94	11,700[a]	52	2.0[c]
21	83	8600[b]	51	1.8[c]
22	89	8200[b]	58	2.0[c]
23	---	15,800[a]	40	1.9[c]

Refer to Table 3.1 for polymer structures.
a: Determined by NMR endgroup analysis.
b: Determined by VPO.
c: Molecular weight distribution determined using unprecipitated reaction mixture by gel permeation chromatography relative to polystyrene.

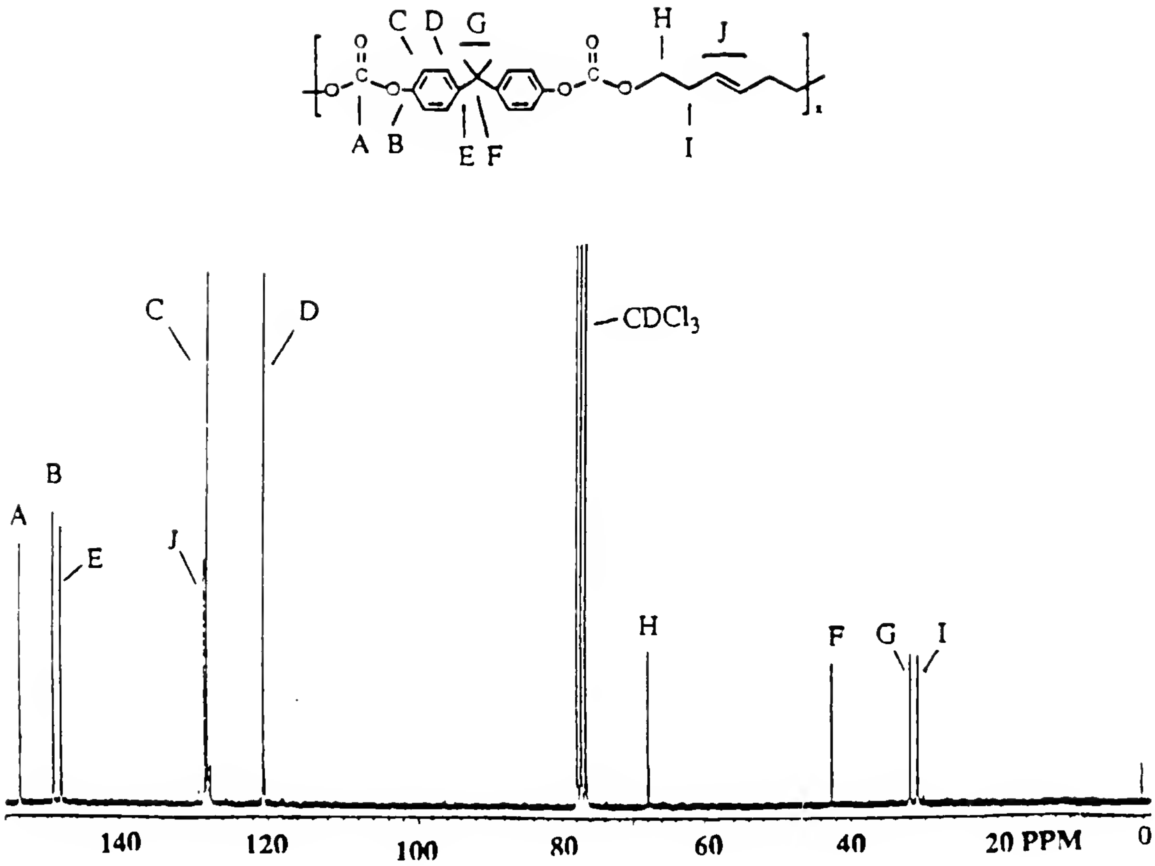


Figure 3.5. ^{13}C NMR for polymer 23 obtained using a 200 MHz instrument and $CDCl_3$ as the solvent.

for the presence of the lower molecular weight fractions. In the case of polymer 23 evidence of lower molecular weight cyclics was observed both in the GPC trace as well as in the thermal analysis. A polymerization of monomer 19 in a dilute solution enhanced the formation of cyclics (Figure 3.6). The major product was again high molecular weight polymer, however, significant fractions of low molecular weight compounds were also evident. The ^{1}H and ^{13}C NMR spectra of this material revealed the absence of vinyl

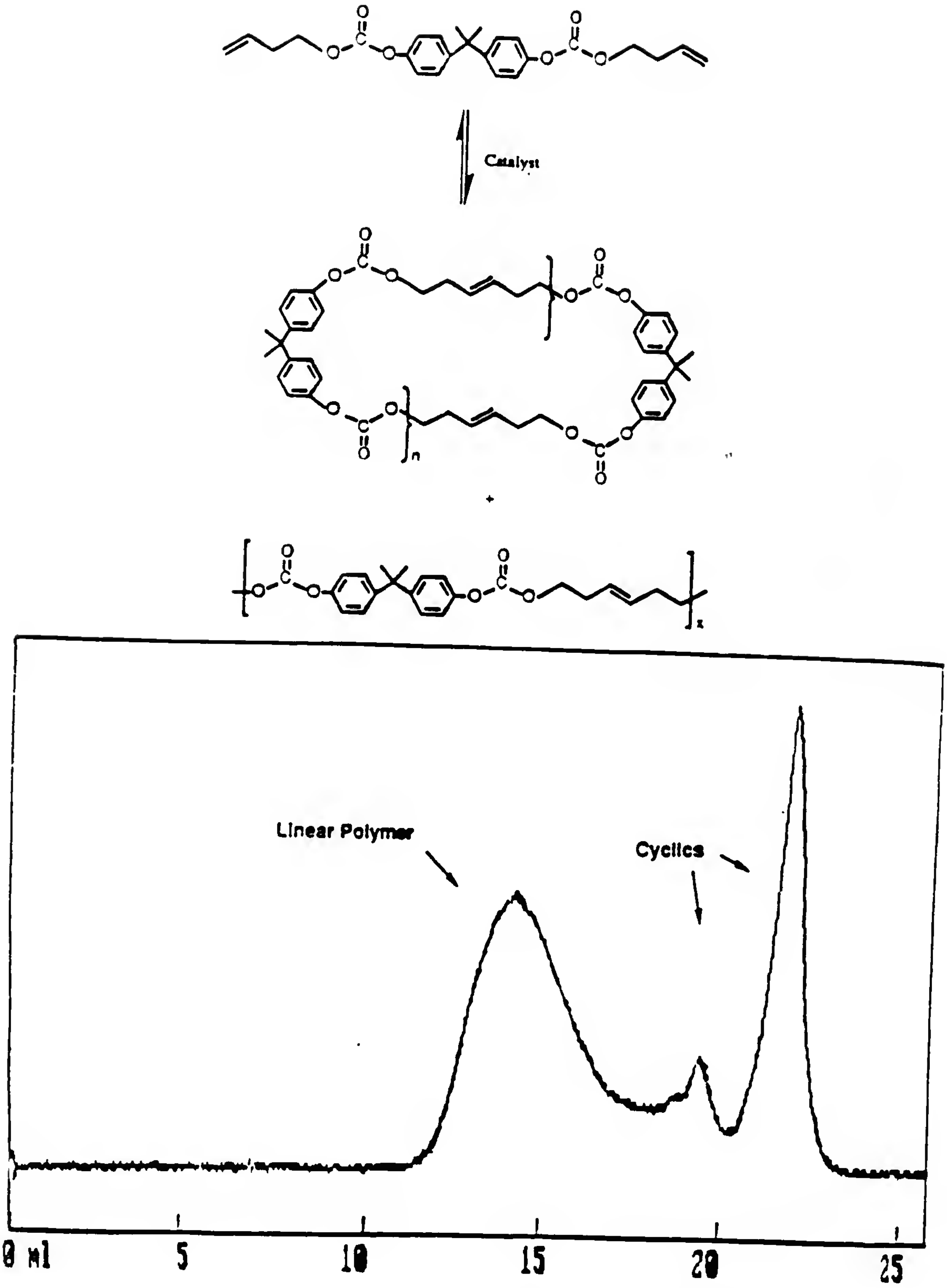


Figure 3.6. GPC trace demonstrating the presence of low molecular weight oligomers with the elution times being relative to polystyrene and THF as the solvent.

endgroups which are easily observed in ADMET polymerizations up to a degree of polymerization of approximately 50 for linear chains.

Thermal Analysis of the Unsaturated Polycarbonates

The thermogravimetric analysis (TGA) data is shown in Table 3.3. Polymers 20-22 exhibited a large initial weight loss in a single step. Polymer 23 showed an initial weight loss at 75°C, however, only 5% weight loss was observed up to 275°C at which time a large weight loss was observed (Figure 3.7). The reason for this initial weight loss is presumably due to the presence of lower molecular weight cyclics which are decomposing at lower temperatures than the high molecular weight fraction.

The differential scanning calorimetry (DSC) data is shown in Table 3.4. No T_g is observed for polymers 20 and 22 above -100°C. Polymer 21 showed a T_g at -58°C for a 5°C/min. ramp rate. No other transitions were observed between 150 and -100°C for this polymer, however, due to the slow kinetics of crystallization. Polymer 23 was measured between -100°C and 60°C (Figure 3.8). The initial heating cycle showed a clear T_m after which the only resolvable and reproducible transition was that of the T_g, due to the slow kinetics of crystallization or possibly a trace amount of cyclics not removed in the purification step.

Table 3.3. Thermogravimetric analysis data for unsaturated polycarbonates.

Polymer	Onset (°C)		90 % Weight Loss (°C)	
	Air	Nitrogen	Air	Nitrogen
20	222	230	455	360
21	235	271	445	414
22	222	255	495	460
23	70	75	490	445

Refer to Table 3.1 for polymer structures. All values obtained at a 5°C/min. heating rate.

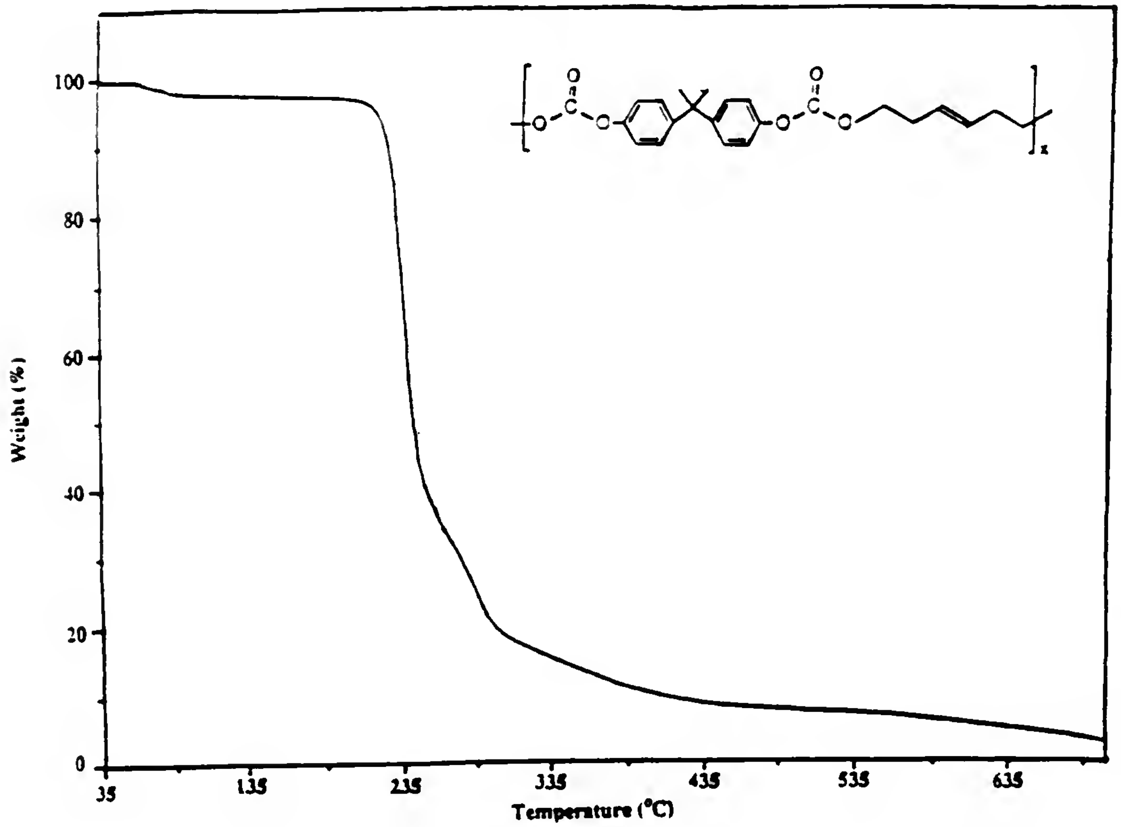


Figure 3.7. TGA thermogram for polymer 23 obtained at a 5°C/min. heating rate under a nitrogen purge.

Table 3.4. Differential scanning calorimetry data for unsaturated polycarbonates.

Polymer	T_m (°C)	T_c (°C)	T_g (°C)
20	77.8^{a}	57.5^{a}	--------
21	--------	--------	-58.0^{b}
22	42.2^{a}	31.5^{a}	-------
23	29.5^{a}	--------	-21.9^{a}

Refer to Table 3.1 for polymer structures. T_g is defined as the glass transition temperature, T_c as the temperature of crystallization, and T_m as the melting temperature.

a: Values obtained at 20, 10, and 5°C/min. and then extrapolated back to 0°C/min.

b: Values determined from 5°C/min. cycle.

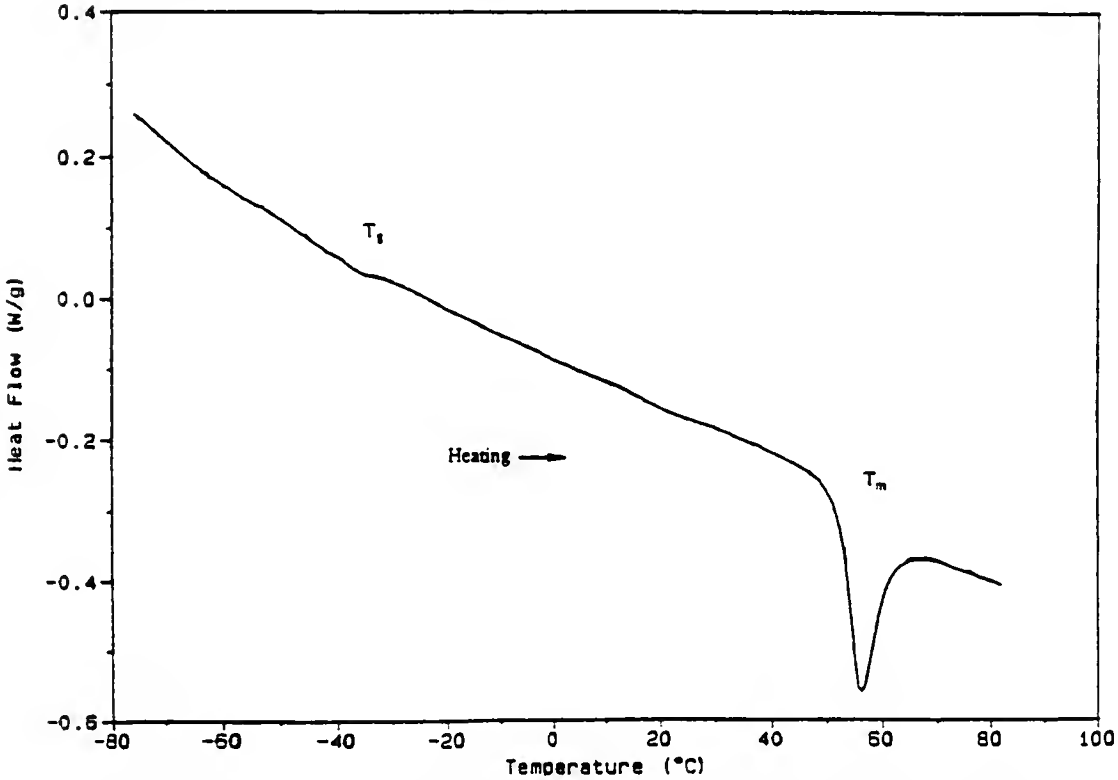


Figure 3.8. DSC thermogram for polymer 23 obtained from a 5°C/min. heating rate under a nitrogen purge.

Acyclic diene metathesis (ADMET) polymerization offers a viable route for the synthesis of pure unsaturated polycarbonates. The use of the highly active, Mo based, Lewis acid-free alkylidene catalyst, 1a, provides a clean route to unsaturated polycarbonates with known vinyl endgroups. The polymerizability of a monomer is limited by the number of methylene spacers between the carbonate functionality and the olefin, a phenomenon which we term the negative neighboring group effect, which was first observed in the case of the ester functionality. The successful polymerization of the ester and carbonate containing dienes demonstrates that these functionalities can be metathesized without the interference of Wittig-type chemistry. This led to the investigation of ketone containing dienes since this functionality is more susceptible to Wittig type chemistry than the ester or carbonate groups.

CHAPTER 4

ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION: THE SYNTHESIS OF UNSATURATED POLYKETONES

This chapter reports the successful synthesis of unsaturated polyketones via the ADMET polymerization using the molybdenum based catalyst $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$, 1a. Unsaturated polyketones were not known prior to this work, and the ADMET polymerization of ketone containing dienes completes an investigation of the ADMET polymerization of carbonyl containing monomers. The successful ADMET polymerization of ester and carbonate containing dienes is described in previous chapters.

The preparation of saturated polyketones is well established, as is the case for polyesters and polycarbonates, and at least three synthetic routes to saturated polyketones are known (Figure 4.1).[53] Reaction 4.1.1 is generally initiated via free-radical chemistry to produce random or alternating copolymers or by a nickel catalyst resulting in perfectly alternating copolymers.[53,54] Reaction 4.1.2 is carried out under basic conditions demonstrating one of the few examples of nucleophilic aromatic substitution successfully used in polymer chemistry.[55,56] Reaction 4.1.3 is performed under Friedel-Crafts conditions which is also rarely successful in polymer

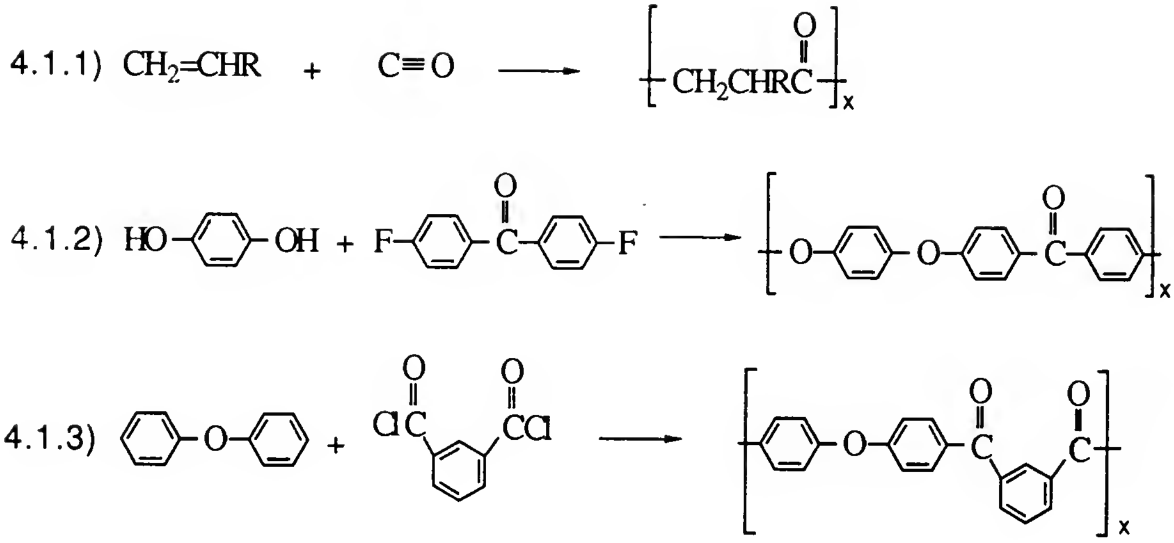


Figure 4.1. Conventional syntheses of polyketones.

chemistry.[57,58] While these methods of polymer synthesis are rare, nonetheless, these saturated polymers are successfully synthesized and commercially important.

Synthesis of Unsaturated Polyketones

Acyclic diene metathesis (ADMET) polymerization augments the chemistry discussed above by allowing the synthesis of unsaturated polyketones.[59] These ketone containing monomers were interesting since the ketone functionality is more susceptible to the Wittig type chemistry previously described (Figure 1.10) than the ester or carbonate functionalities.

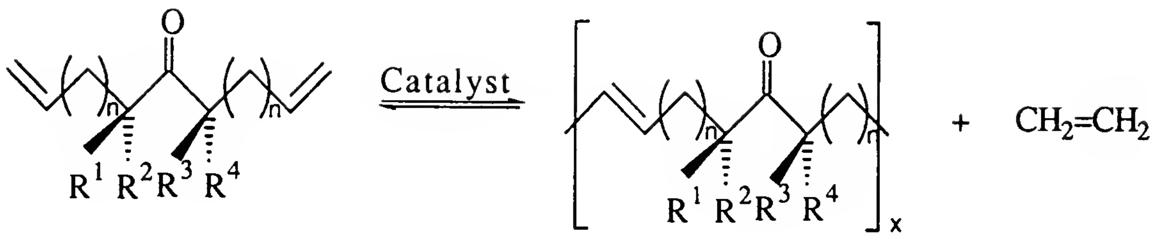
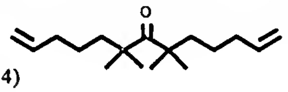
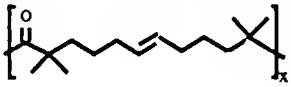
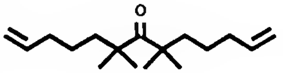
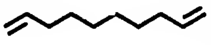
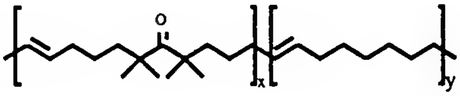
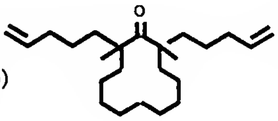
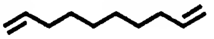
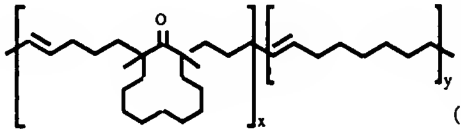
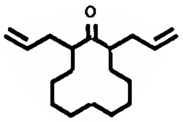
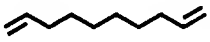
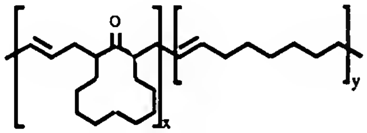
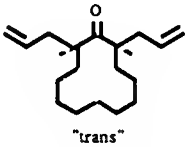
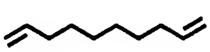
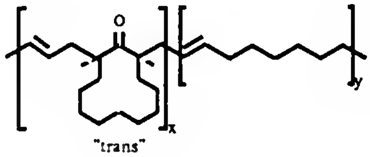


Figure 4.2. ADMET polymerization of tetraalkyl-keto-dienes.

Both homopolymerizations and copolymerizations have been used in this research to synthesize the unsaturated polyketones (Table 4.1). The homopolymerization of 24 resulted in the violent evolution of ethylene as the rapid polymerization to 29 occurred. Wittig-type chemistry does not interfere, likely due to steric hinderence around the carbonyl group due to the presence of the methyl groups. Evidence for this successful polymerization can be seen in the conversion of monomer 27 to polymer 32 demonstrating the ability to synthesize high molecular weight polymers. Monomer 27 does not possess the methyl groups and is therefore less sterically hindered about the carbonyl group and, as shown in Table 4.2, there is a very large decrease in the molecular weight for this polymer.

Unsaturated polyketone copolymers were successfully obtained via the copolymerization of 1,9-decadiene with a variety of comonomers, and summary of the monomers studied and the polymers formed is found in Table 4.1. These copolymerizations proceed rapidly and exhibit no evidence of chain transfer or branching in either the ^1H NMR or ^{13}C NMR. The polymers formed also exhibit the optimal molecular weight distribution (MWD) of 2.0

Table 4.1. Unsaturated polyketones synthesizes via the ADMET polymerization.

Monomer		Polymer
X	Y	
(24) 	----	 (29)
(25) 		 (30)
(26) 		 (31)
(27) 		 (32)
(28) 		 (33)

which is the expected value for clean step polymerizations. These reactions demonstrate the ability to rapidly synthesize high molecular weight unsaturated polyketones.

Unsaturated Polyketone Characterization and Molecular Weight Analysis

Table 4.2 compiles the molecular weight and structural data for polymers 29-33. In all cases, the oligomers were found to be perfectly linear and pure demonstrating that unsaturated polyketones with steric bulk around the carbonyl group can be successfully synthesized using the ADMET polymerization The *trans/cis* ratio found in polymers 29-33 was similar to that observed for other ADMET polymers.[34] The lower molecular weights of polymers 32 and 33 was likely due to the presence of trace amounts of mono-ene present in the reaction mixture.

Table 4.2. Molecular weight data for unsaturated polyketones.

Polymer	Y/X	$\bar{X}_n$ [a]	$\bar{M}_n$ [a]	$\bar{M}_w$ [b]	MWD [b]
29	----	>50	----	16,400	1.7
30	1/1	>50	----	30,600	1.7
31	6/1	13	----	5,000	2.0
32	6/1	5	640	----	1.9
33	5/1	13	1,760	4,900	1.8

a: Determined by endgroup analysis from ^1H NMR.
b: Determined by gel permeation chromatography relative to polystyrene.

ADMET Cyclization of Ketone Containing Dienes

The attempted homopolymerization of compounds 34 and 35 produced an intriguing set of results. Rather than giving the expected linear polymers, they were found to quantitatively cyclize in the absence of solvent to give difunctional seven membered rings (Figure 4.3). Molecular mechanics (MM2) calculations support the hypothesis that the Thorpe-Ingold effect, due to two pairs of gem-dimethyl groups adjacent to the carbonyl carbon, is forcing the linear ketononadiene into a horseshoe conformation inducing cyclization.[60,61]

Examples of substituted diene cyclizations by metathesis, even in the presence of a solvent, are rare.[62] A silacyclopentene ring has been formed in low yield using an aluminum/rhenium catalyst system, and five and six membered rings have been formed in the intramolecular reaction of a tungsten carbene complex, where the diene was one of the ligands.[63,64] Cyclization of unsubstituted 1, 7-dienes in various solvents has been reported, but complete conversion occurs only in a few cases.[1,65,66] Formation of cyclic alkene oligomers from back-biting during the ROMP reaction is also known.[67] These cyclizations are unusual in that they are intermolecular between catalyst and substrate and yield quantita-

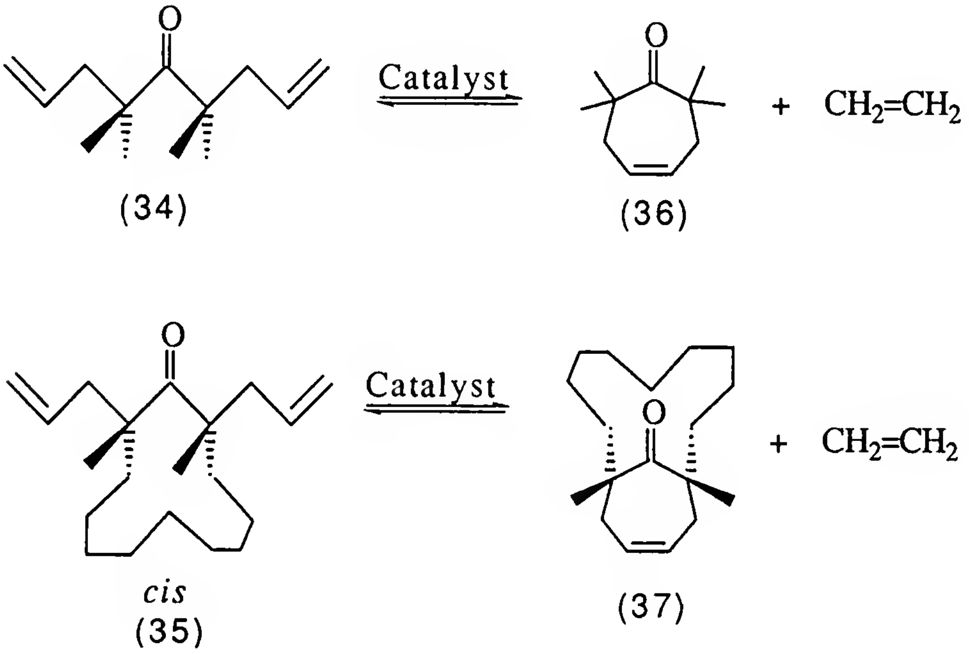


Figure 4.3. ADMET cyclization of Tetraalkyl-5-keto-1,8-nonadienes.

tive product solely from the monomer in the absence of solvent. The dilute solution cyclization of ether containing dienes to five, six, and seven-membered rings has recently been reported in which, again, substitution alpha to the heteroatom is present implying a Thorpe-Ingold effect.[62]

Ketodiene 34 cyclized to give tetramethylcycloheptanone 36 quantitatively in one hour total reaction time (Figure 4.3). The ^{1}H NMR of the cyclization of 34 is presented in Figure 4.4. An attempt to copolymerize 34 with 1,9-decadiene yielded the entire amount of 34 cyclized while the 1,9-decadiene underwent an independent ADMET homopolymerization to polyoctenomer. The polymer could be separated from 36 by precipitation into methanol. The longer diene 29 (see Table 4.1), however, gave only polymer, indicating that a fairly rigid conformation of the diene is necessary for cyclization. The unmethylated ketone 38 gave only a mixture of linear oligomers in an NMR reaction (Figure 4.5). Cyclic ketodiene 35 also gave quantitative cyclization to the unusual bicyclic ketoalkene 37 in a solventless reaction in one hour (Figure 4.3). As in the linear case, the longer diene 26 (see Table 4.1) gave only linear oligomers under the same reaction conditions.

These results suggest that the cyclization is brought about by the Thorpe-Ingold effect as previously mentioned.[68-70] MM2 calculations were run in order to find the local conformational energy conditions.[61] The two conformers of 34 are shown in Figure 4.6. Conformer 34a was found to be favored by 2.9 kcal/mole with the distance between the terminal carbon atoms being 3.5 A, while in 34b it is 9.3 A. This may explain why cyclization takes place in the absence of solvent, and why the attempted copolymerization was unsuccessful. In the case of the unmethylated ketone 38, the analogous conformers were found to be isoenergetic within 0.1 kcal/mole. If the first metathesis reaction occurs after approach of the catalyst to the outside of the horseshoe, only a single bond rotation is required to bring the metal into close contact with the olefin moiety on the other side.

Mono-gem-disubstituted compounds were investigated in an attempt to further demonstrate the potential synthetic utility of these cyclizations (Figure 4.7). These compounds further support the hypothesis that with the appropriate substitution cyclization can be induced.

The cyclizations were performed using very small amounts of reactants making it difficult to determine the true overall yield possible. The use of NMR and GC/MS, however, verified that only cyclized compound and no oligomerized product was present in the cases of reactants 42, 43, 44, and 46. The attempted cyclization of reactant 44 in a NMR reaction resulted in only linear polymer with a degree of polymerization of at least 50 repeat units in ten minutes. The rate of the polymerization under the dilute NMR conditions indicates that cyclization is likely occurring followed by the rapid ring opening metathesis polymerization (ROMP) of the cyclic compound.

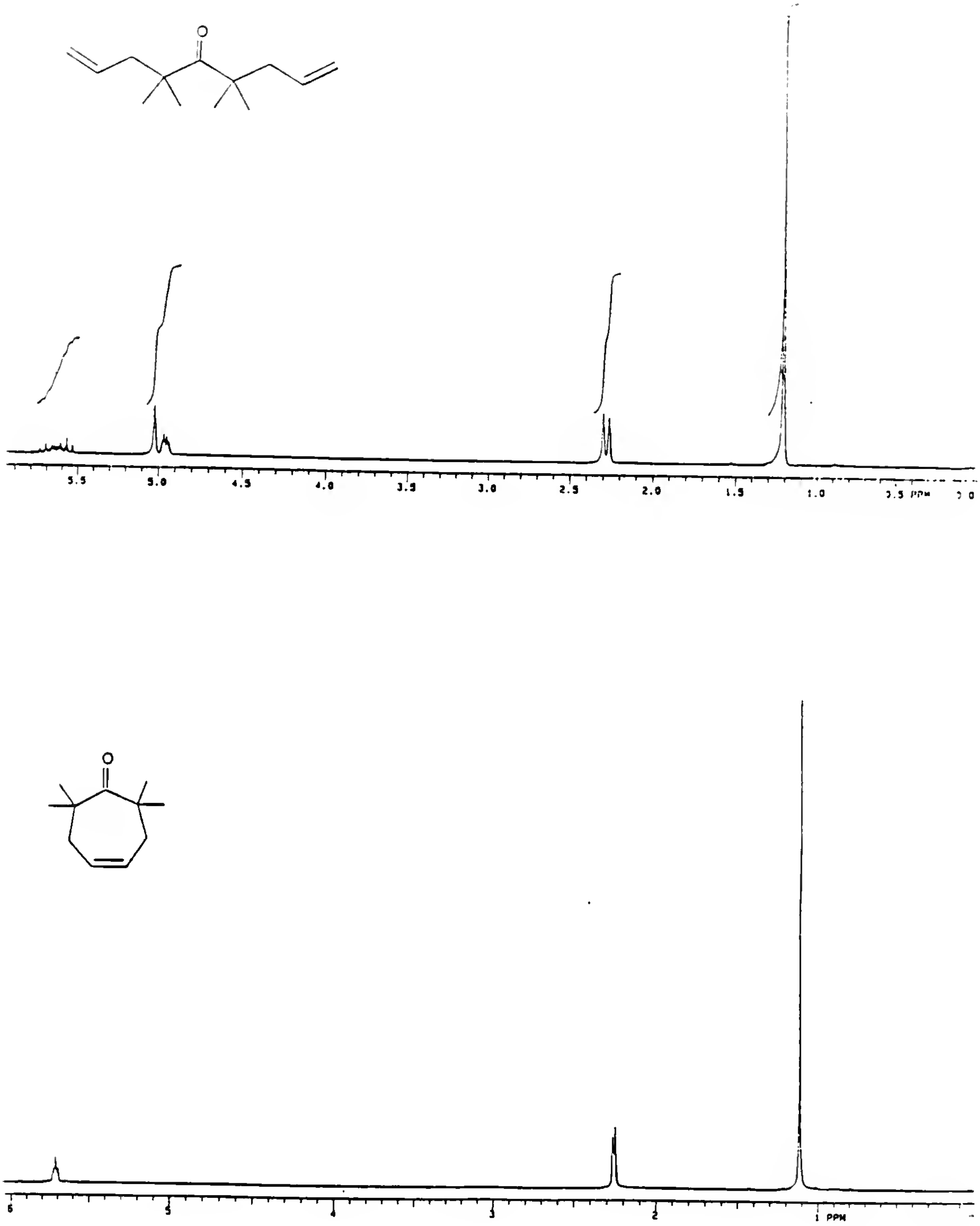


Figure 4.4. ^{1}H NMR of the cyclization of 34 to 36 after one hour performed under drybox conditions.

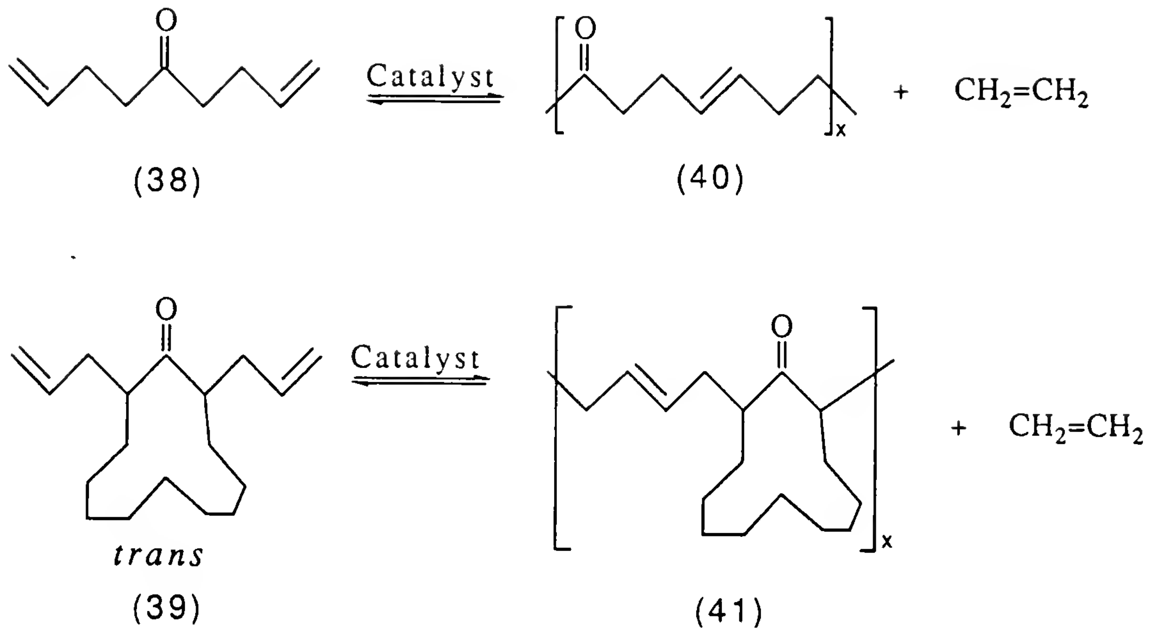
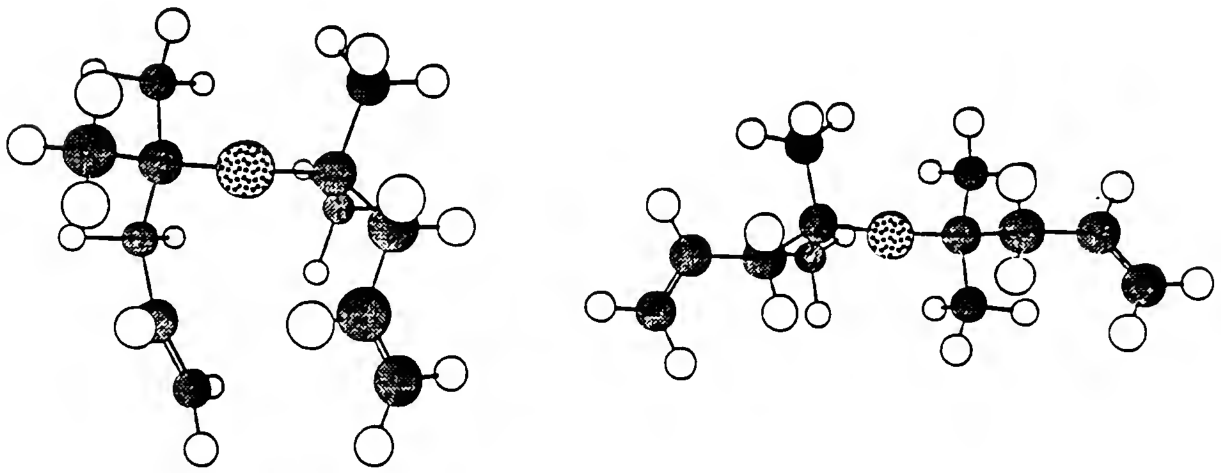

Catalyst
+ CH2=CH2
(38)
(40)
Catalyst
trans
(39)
+ CH2=CH2
(41)

Figure 4.5. Linear oligomerization of unmethylated keto-dienes.



34a

34b

Figure 4.6. "Horseshoe" and "crescent" conformers of 34.

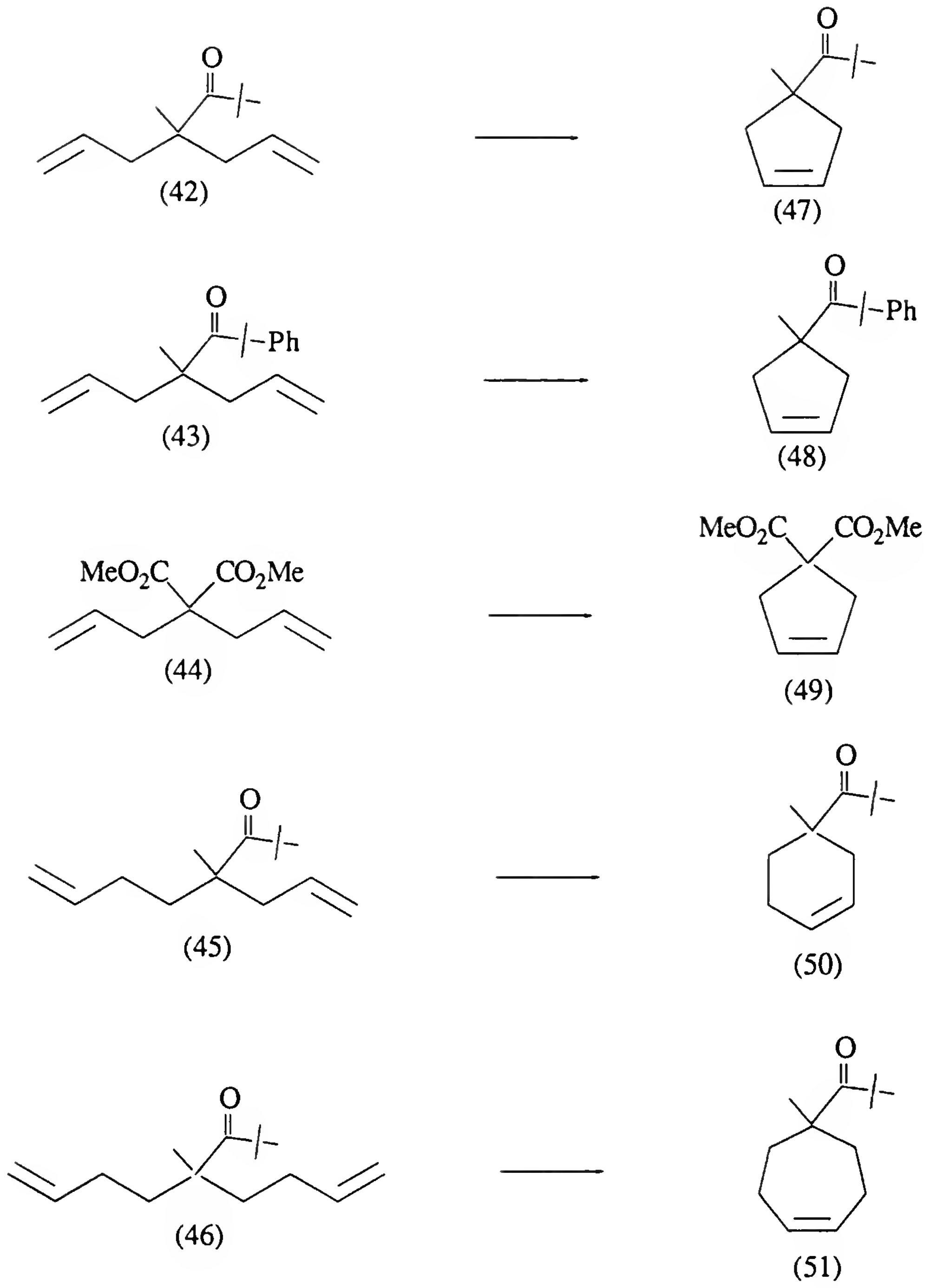

O
Ph
MeO2C
CO2Me
(42)
(47)
(43)
(48)
(44)
(49)
(45)
(50)
(46)
(51)

Figure 4.7. Cyclization of mono-gem-disubstituted compounds.

Summary

The use of the highly active, Mo based, Lewis acid-free alkylidene catalyst, 1a, provides a clean route to unsaturated polyketones as well as polyesters and polycarbonates with known vinyl endgroups. This demonstrates the fact that the ADMET polymerization may be utilized even in cases where highly polar functional groups such as the carbonyl functionality are present. These polymerizations were used to study structure control in the repeat unit and structure reactivity relationships.

In terms of the structure reactivity relationships of monomers the ADMET synthesis of unsaturated polyesters and polycarbonates exhibits a negative neighboring group effect. This negative neighboring group effect involves either the coordination of the carbonyl oxygen to the metal center or simply the polarization of the double bond such that the intermediates of the metathesis process are not favored. While this phenomenon has not been studied for the ketone containing dienes it is likely that the same effect would be observed.

Ketone containing dienes were shown to cyclize at very high conversions when the appropriate substitutions are present. The reason for the cyclizations is due to a Thorpe-Ingold effect where the diene exists in a conformer which favors cyclization. These cyclizations are a potentially powerful tool in the area of synthesis.

CHAPTER 5

EXPERIMENTAL

Monomer syntheses were performed under dry argon atmosphere using standard Schlenk techniques. Toluene and pentane were extracted with cold concentrated sulfuric acid followed by basic potassium permanganate. Tetrahydrofuran (THF), pentane, and toluene were distilled from potassium benzophenone ketyl. The compounds $Mo(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$ and $W(CHCMe_2R)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCCH_3(CF_3)_2]_2$, 1 and 2 (Figure 2), were prepared according to literature methods.[19,71] All other solvents and reagents were purged with argon and used without further purification.

The ketone containing dienes 24-28, 34-35, 38-39, and 42-46 were synthesised by Dr. Malcolm Forbes and were used without further purification.[59] A sample synthesis of these ketones can be seen in the synthesis of 4,4,6,6-tetramethyl-1,8-nonadiene-5-one, 34.

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-300 (300 MHz) or a Varian XL-200 (200 MHz) spectrometer. NMR data are listed as parts per million downfield from TMS. Obvious multiplicities and routine coupling constants are not listed.

NMR spectra are obtained in $CDCl_3$ unless otherwise noted. IR data was recorded on a Perkin Elmer 281 Infrared Spectrometer. Gel permeation chromatography (GPC) analyses were carried out with the use of Phenomenex Phenogel 5 500A and 5000A columns coupled, a Waters Associates differential refractometer, and a Perkin-Elmer LC-75 spectrophotometric detector on polymer samples 0.1-0.3 % W/V in THF. The GPC columns were calibrated versus commercially available polystyrene samples ranging from 910 to 1.10×10^5 g/mole. Vapor pressure osmometry was carried out with the use of a Wescam 233 molecular weight apparatus at 50°C on polymer samples ranging from 8 to 18 g/L in toluene. Differential scanning calorimetry (DSC) was carried out using a DuPont DSC 2910 Differential Scanning Calorimeter. Thermogravimetric analysis (TGA) was carried out using a DuPont Hi-Res TGA 2950 Thermogravimetric Analyzer. Elemental analyses are by Atlantic Microlab, Inc., Atlanta, GA.

1,4 Benzene dicarboxylic bis (1-hexenyl) ester (3). Terephthaloyl chloride (5.0 g, 0.025 moles) was purged with argon and then dissolved in 50 mL of dry THF followed by the dropwise addition of dry pyridine (3.90 g, 0.050 moles, exothermic) via a syringe. 5-Hexene-1-ol (10.0 g, 0.10 moles) was added dropwise via a syringe after which the mixture was heated to reflux for 3 hours under argon. The THF was removed in vacuo. The residue was dissolved in 50 mL of H_2O and washed with 100 mL of diethyl ether. The ether fractions were combined, washed once with 10% aqueous HCl, and washed twice with 10% aqueous Na_2CO_3. Initial distillation via short path distillation under full vacuum yielded the product as a colorless oil (8.79 g, 92 %). Further purification for polymerization of 3 was accomplished by distillation via short path distillation under full vacuum onto CaH_2 and stirred overnight followed by filtration of the monomer through a celite bed with the aid of pentane after which the pentane was removed in vacuo. The monomer was then redistilled via short path distillation under full vacuum into a roundbottom storage flask equipped with a Rotaflow stopcock and molecular sieves. It had the following spectral properties, ^1H NMR ($CDCl_3$), 1.54 (p, 2 H), 1.79 (p, 2 H), 2.12 (q, 2 H), 4.33 (t, 2 H), 4.91-5.10 (m, 2 H), 5.69-5.92 (m, 1 H), 8.08 (s, 2 H); ^{13}C NMR ($CDCl_3$), 166.0, 138.2, 134.1, 129.1, 115.1, 65.5, 33.2, 27.8, 25.2. The IR spectrum (neat, KBr) showed absorptions at: 2850, 1710, 1405, 1265 cm^{-1}. Anal. Calcd. for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.79; H, 7.95.

1,4 Benzene dicarboxylic bis (1-pentenyl) ester (4). Preparation of 4 from terephthaloyl chloride (5.0 g, 0.025 moles), pyridine (3.90 g, 0.050 moles), and 4-penten-1-ol (4.32 g, 0.050 moles) was analogous to the procedure for 3 yielding the product as a colorless oil (6.44 g, 94 %) with the following spectral properties: ^1H NMR ($CDCl_3$), 1.88 (p, 2 H), 2.21 (q, 2 H), 4.35 (t, 2 H), 4.95-5.14 (m, 2 H), 5.72-5.97 (m, 1 H), 8.08 (s, 2 H); ^{13}C NMR ($CDCl_3$), 166.0, 137.8, 134.1, 129.8, 115.7, 64.9, 30.0, 28.0. The IR spectrum (neat, KBr) showed absorptions at: 2850, 1715, 1405, 1265 cm^{-1}. Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 71.38; H, 7.31.

1,4 Benzene dicarboxylic bis(1-butenyl) ester (5). Preparation of 5 from teraphthaloyl chloride (12.50 g, 0.0246 moles), pyridine (9.81 g, 0.124 moles), and 1-butenol (10.0 g, 0.139 moles) was analogous to the procedure for 3 yielding the product as a colorless oil (15.03 g, 89 %) with the following spectral properties: ^{1}H NMR (CDCl3), 2.50 (q, 2 H), 4.37 (t, 2 H), 5.02-5.21 (m, 2 H), 5.72-5.97 (m, 1 H), 8.08 (s, 2 H); ^{13} C NMR (CDCl3) 165.9, 134.0, 133.9, 129.9, 117.6, 64.2, 33.1. The IR spectrum (neat, KBr) showed absorptions at: 2900, 1720, 1640, 1405, 1265 cm^{-1}. Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 69.96; H, 6.65.

1,4 Benzene dicarboxylic bis (1-propenyl) ester (6). Preparation of 6 from teraphthaloyl chloride (5.0 g, 0.025 moles), pyridine (3.9 g, 0.05 moles), and allyl alcohol (3.9 g, 0.05 moles) was analogous to the procedure for 3 yielding the product as a colorless oil (5.27 g, 87 %) with the following spectral properties: ^{1}H NMR (CDCl3), 4.83 (dd, 2 H), 5.24-5.48 (m, 2 H), 5.92-6.15 (m, 1 H), 8.11 (s, 2 H); ^{13} C NMR (CDCl3) 165.7, 134.1, 132.0, 129.9, 118.9, 66.0. The IR spectrum (neat, KBr) showed absorptions at: 2800, 1720, 1650, 1405, 1265 cm^{-1}. Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.15; H, 5.66.

1-Hexene-1-pentenoate (7). 1-Pentenoic acid (10.0 g, 0.10 moles), 5-hexene-1-ol (9.0 g, 0.090 moles), and 5 drops of concentrated H_2SO_4 were refluxed in 150 mL of benzene in a Dean-Stark apparatus for 12 hours with the occasional removal of H_2O. The benzene was removed *in vacuo*, and the remaining oil was mixed with 50 mL of diethyl ether and washed with a 10% Na_2CO_3 solution (3 x 50mL) followed by one wash with a NaCl solution. The ether solution was dried over $MgSO_4$, filtered, and the ether removed in vacuo. The resulting oil was then distilled via short path distillation under a static vacuum into a flask containing CaH_2 and stirred for 12 hours. The mixture was filtered through a celite bed with the aid of pentane after which the pentane was removed *in vacuo*. The colorless oil was redistilled via short path distillation under static vacuum into a storage flask equipped with a Rotaflow stopcock and molecular sieves (14.75 g, 81 %) with the following spectral properties: ^1H NMR ($CDCl_3$), 1.47-1.54 (m, 1 H), 1.54-1.71 (m, 1 H), 2.07 (q, 1 H), 2.38 (s, 2 H), 4.07 (t, 1 H), 4.84-5.11 (m, 2 H), 5.67-5.92 (m, 1 H); ^{13}C NMR ($CDCl_3$) 173.2, 138.5, 136.9, 128.6, 115.6, 114.8, 64.2, 33.8, 33.6, 29.6, 28.3, 25.8. The IR spectrum (neat, KBr) showed absorptions at: 2850, 1735, 1640, 1170 cm^{-1} Anal. Calcd. for $C_{11}H_{18}O_4$: C, 72.49; H, 9.95. Found: C, 72.48; H, 9.92.

1-Hexene-1-butenoate (8). Preparation of 8 from vinyl acetic acid (5.0 g, 0.058 moles), 5-hexene-1-ol (5.23 g, 0.052 moles), and 5 drops of concentrated H_2SO_4 was analogous to the procedure for 7 yielding the product as a colorless oil (7.53 g, 77 %) with the following spectral properties: ^1H NMR ($CDCl_3$), 1.37-1.52 (m, 1 H), 1.52-1.72 (m, 1 H), 1.98-2.16 (q, 1 H), 3.01-3.16 (d, 1 H), 4.00-4.19 (t, 1 H), 4.90-5.26 (m, 2 H), 5.68-6.04 (m, 1 H); ^{13}C NMR ($CDCl_3$) 171.8, 138.1, 130.9, 128.3, 118.5, 115.1, 65.0, 39.4, 33.2, 28.0, 25.2. The IR spectrum (neat, KBr) showed absorptions at: 2850, 1740, 1640, 1070 cm^{-1} Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.38; H, 9.59. Found: C, 71.10; H, 9.64.

Poly(oxy-5-decene-oxyteraphthaloyl) (9). In a nitrogen filled drybox, 1a (0.01 g, 1.54 x 10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock and two addition arms with breakseals for additional catalyst additions. Each of the breakseal containers was charged with 1a (0.005 g, 7.67 x 10^{-6} moles) dissolved in 1.5 mL of toluene. Compound 3 (2.0 g, 6.05 x 10^{-3} moles) was then added to the catalyst in the Schlenk tube and the mixture stirred. Rapid evolution of ethylene was observed and the reaction mixture became solid within 5 minutes. Toluene (20mL) was then added to the mixture which was then sealed, removed from the drybox, and attached to a vacuum line where the system was exposed to a slight vacuum to aid in the removal of ethylene. The reaction mixture was then slowly warmed to 45°C and allowed to stir under a static vacuum. At 3 hour intervals, each of the 2 breakseals were broken. The initial catalyst to monomer ratio was 400:1. Three hours after the second catalyst addition, compound 9 was purified by dissolution in warm toluene followed by the dropwise addition of the polymer solution into rapidly stirring methanol at 0°C. The white precipitate was then separated from the solvents by centrifugation followed by the decanting of the solvents yielding 9 as a white powder (1.66 g, 92 %) with the following spectral properties: ^{1}H NMR (200 MHz, $CDCl_3$), 1.54 (p, 2 H), 1.79 (p, 2 H), 2.12 (q; 2 H), 4.33 (t, 2 H), 4.91-5.10 (m, 2

H), 5.38-5.49 (br, 1 H), 5.69-5.92 (m, 1 H), 8.08 (s, 2 H); ^{13}C NMR (50 MHz, $CDCl_3$) 166.0, 134.3, 130.4, 129.8, 129.7, 65.5, 32.0, 28.1, 25.9. The IR spectrum (film, KBr) showed absorptions at: 2825, 1705, 1450, 1265 cm^{-1} Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.33. Found: C, 68.79; H, 7.41.

Room Temperature Synthesis of 9. In a drybox equipped with nitrogen atmosphere 1a (0.01 g, 1.53 x 10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock followed by 3 (2.0 g, 6.05 x 10^{-3} moles). Rapid evolution of ethylene was observed and the reaction mixture became solid within 5 minutes. The solid was then dissolved in 20 mL of toluene and allowed to stir for an additional 8 hours in a closed reaction vessel. The oligomers were purified as in the 45 °C case (1.74 g, 95 %).

Poly(oxy-4-octene-oxyteraphthaloyl) (10). Preparation of 10 from 1a (0.011 g, 1.65 x 10^{-5} moles) in the Schlenk tube and 1a (0.005 g, 7.67 x 10^{-6} moles) in each of the 2 breakseals was analogous to the procedure for 9 (45 °C case) with 4 (2.0 g, 0.00661 moles) to yield 10 as a white powder (1.53 g, 94 %) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.88 (p, 2 H), 2.21 (br, 2 H), 4.35 (t, 2 H), 4.95-5.14 (m, 2 H), 5.45-5.57 (br, 1 H), 5.72-5.97 (m, 1 H), 8.08 (s, 4 H); ^{13}C NMR ($CDCl_3$) 166.0, 134.2, 130.0, 129.8, 65.0, 28.9, 28.5. The IR spectrum (film, KBr) showed absorptions at: 2875, 1710, 1445, 1265 cm^{-1} Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.06; H, 6.61. Found: C, 68.40; H, 6.70.

Poly(oxy-3-hexene-oxyteraphthaloyl) (11). Preparation of 11 from 1a (0.012 g, 1.82×10^{-5} moles) in the Schlenk tube and 1a (0.005 g, 7.67×10^{-6} moles) in each of the 2 breakseals was analogous to the procedure for 9 with 5 (2.0 g, 0.00729 moles) to yield poly(oxy-3-hexene-oxyteraphthaloyl) as a white powder (1.62 g, 90 %) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 2.40-2.65 (br, 2 H), 4.4.25-4.45 (t, 2 H), 5.57-5.73 (br, 1 H), 7.95-8.15 (s, 2 H); ^{13}C NMR ($CDCl_3$) 165.9, 134.1, 129.8, 128.7, 126.9, 64.6, 32.1. The IR spectrum (film, KBr) showed absorptions at: 3100, 1705, 1405, 1250 cm^{-1} Anal. Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 66.23; H, 5.73.

Poly[oxy-(3-octene)-ester] (12). In a drybox equipped with nitrogen atmosphere 1a (0.018 g, 2.74×10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock followed by 7 (2.0 g, 0.011 moles). Rapid evolution of ethylene was evident and the reaction was allowed to stir until the reaction mixture became too thick to stir after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 hours (1.68 g, 99%). It had the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.37-1.52 (m, 1 H), 1.52-1.72 (m, 1 H), 1.92 - 2.16 (br, 1 H), 2.16-2.50 (br, 2 H), 3.93-4.20 (t, 1 H), 5.27-5.60 (br, 1 H); ^{13}C NMR ($CDCl_3$) 173.4, 131.2, 130.4, 129.6, 128.8, 64.4, 34.3, 34.2, 32.2, 28.1, 28.0, 26.0, 25.9. The IR spectrum (film, KBr) showed absorptions at: 2725, 1735, 1160, 965 cm^{-1} Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.18; H, 9.18.

Attempted polymerization of (8). 1a (0.019 g, 2.97 x 10^{-5} moles) and 8 (2.0 g, 0.012 moles) were reacted in an analogous procedure for the synthesis of 12. Upon addition of the monomer to the catalyst there was no apparent evolution of ethylene and after 3 hours ^{1}H NMR revealed only unreacted starting material.

Copolymerization of 4 and 1,9-Decadiene (13). 4 (0.50 g, 0.0017 moles) and 1,9-decadiene (0.22 g, 0.00165 moles) were mixed together and then added to a Schlenk tube preloaded with 1a (0.005 g, 8.27 x 10^{-6} moles). Rapid evolution of ethylene was observed. Within 15 minutes the reaction mixture went solid after which 20 mL of toluene was added to dissolve the mixture which was then allowed to stir for an additional 8 hours. The reaction flask was then removed from the drybox and the polymer purified as described for the aromatic homopolymers. It had the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.18-1.45 (s, 2 H), 1.72-2.08 (m, 1 H), 4.23-4.41 (t, 1 H), 5.27-5.56 (m, 1 H), 8.02-8.17 (s, 1 H); ^{13}C NMR ($CDCl_3$), 166.0, 134.2, 131.9, 130.2, 130.0, 129.6, 129.2, 128.7, 128.3, 128.0, 125.5, 64.5, 32.6, 29.8, 29.7, 29.0, 28.9, 28.4, 28.3. The IR spectrum (neat, KBr) showed absorptions at: 2810, 1720, 1410, 1265 cm^{-1} Anal. Calcd. for $C_{24}H_{33}O_4$: C, 74.77; H, 8.63. Found: C, 73.80; H, 8.44.

Benzene carboxylic (1-propenyl) ester (14). Preperation of 14 from benzoyl chloride (10.97 g, 0.0783 moles), pyridine (6.81 g, 0.0861 moles), and allyl alcohol (5.00 g, 0.0861 moles) was analogous to the procedure for 3 yielding the product as a colorless oil (12.1 g, 95%) with the following spectral properties: ^{1}H NMR (d_8-toluene), 4.75-4.90 (m, 2 H), 5.20-5.55 (m, 2 H), 5.80-6.20 (m, 1 H), 7.20-7.50 (m, 3 H), 8.20-8.35 (m, 2 H); ^{13}C NMR (d_8-toluene) 166.6, 138.4, 129.8, 129.4, 118.6, 66.3. The IR spectrum (neat, KBr) showed absorptions at: 3200, 2890, 1725, 1605, 1370 cm^{-1}.

Bis (1-hexenyl) carbonate (15). 5-Hexene-1-ol (10.0 g, 0.0998 moles), dimethylcarbonate (4.047 g, 0.0449 moles), and LiH (0.020 g, 0.00252 moles) were all added to a dry and argon purged 100 mL roundbottom flask equipped with a flash distillation apparatus. Methanol was then distilled from the mixture under argon until no more methanol was recovered. The flash distillation apparatus was then replaced by a standard fractional distillation apparatus and the fractional distillation continued under vacuum. The product was then stirred over CaH_2 overnight after which the mixture was filtered under argon over a celite bed with the aid of dry pentane. The pentane was then stripped off of the mixture which was then vacuum transferred into a roundbottom storage flask equipped with a Rotaflow stopcock and molecular sieves as a colorless oil (6.61 g, 65%) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.40-1.55 (m, 2 H), 1.64-1.77 (m, 2 H), 2.04-2.17 (q, 2 H), 4.10-4.20 (t, 2 H), 4.93-5.09 (m, 2 H), 5.72-5.88 (m, 1 H); ^{13}C NMR ($CDCl_3$), 155.1, 137.9, 114.5, 67.5, 32.9, 27.8, 24.7. The IR spectrum (neat, KBr) showed absorptions at: 2925, 1750, 1640, 1260 cm^{-1}. Anal. Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.93; H, 9.83.

Bis (1-pentenyl) carbonate (16). Preparation of 16 from 4-pentene-1-ol (10 g, 0.1161 moles), dimethylcarbonate (4.706 g, 0.0522 moles), and LiH (0.02 g, 0.00252 moles) was analogous to the procedure for 15 yielding the product as a colorless oil (6.21 g, 60%) with the following spectral properties: ^1H NMR (CDCl$_3$), 1.72-1.84 (p, 2 H), 2.10-2.21 (p, 2 H), 4.10-4.20 (t, 2 H), 4.96-5.11 (m, 2 H), 5.72-5.89 (m, 1 H); ^{13}C NMR (CDCl$_3$), 155.0, 137.0, 115.1, 67.0, 29.5, 27.5. The IR spectrum (neat, KBr) showed absorptions at: 2960, 1750, 1645, 1260 cm^{-1}. Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.76; H, 9.10.

Bis (1-butenyl) carbonate (17). Preparation of 17 from 3-butene-1-ol (10.0 g, 0.1387 moles), dimethyl carbonate (5.62 g, 0.0624 moles), and LiH (0.02 g, 0.00252 moles) was analogous to the procedure for 15 yielding the product as a colorless oil (7.0 g, 66%) with the following spectral properties: ^1H NMR (CDCl$_3$), 2.39-2.48 (m, 2 H), 4.14-4.23 (t, 2 H), 5.08-5.20 (m, 2 H), 5.72-5.88 (m, 1 H); ^{13}C NMR (CDCl$_3$), 154.8, 133.1, 117.3, 66.5, 32.7. The IR spectrum (neat, KBr) showed absorptions at: 2970, 1750, 1645, 1260 cm^{-1}. Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.56; H, 8.26.

Bis (1-propenyl) carbonate (18). Preparation of 18 from allyl alcohol (10.0 g, 0.1722 moles), dimethylcarbonate (6.97 g, 0.0775 moles), and LiH (0.02 g, 0.00252 moles) was analogous to the procedure for 15 yielding the product as a colorless oil (5.51g, 50%) with the following spectral properties: ^{1}H NMR (CDCl$_3$), 4.53-4.63 (m, 2 H), 5.18-5.40 (m, 2 H), 5.80-6.02 (m, 1 H); ^{13}C NMR (CDCl$_3$), 154.8, 131.5, 118.7, 60.4. The IR spectrum (neat, KBr) showed absorptions at: 2950, 1750, 1650, 1260 cm^{-1}. Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.03; H, 7.10.

1, 4-Phenylene-iso-propylidene-1, 4-phenylene-bis (1-butenyl) carbonate (19). 4-Butene-1-ol (4.94 g, 0.0686 moles) and pyridine (5.42 g, 0.0686 moles) were added to a dry 250 mL Schlenk tube and stirred under argon at 0°C in 50 mL of dry THF. 4, 4'-Isopropylidenediphenol bis (chloroformate) (10.0 g, 0.0286 moles) dissolved in 50 mL of dry THF was then added dropwise via an addition funnel after which the mixture was allowed to stir for an additional 2 hours at room temperature. The solvent was then removed *in vacuo* resulting in a thick yellow oil. The oil was then dissolved in enough toluene to allow transfer by pipet to a 6 inch silica gel column (100-200 mesh) and the product eluted using toluene-hexane (1/1) solvent. The solvent was then removed *in vacuo* and the resulting colorless opaque oil left under vacuum for 8 additional hours to remove any excess 4-butene-1-ol and pyridine. The oil was then dissolved in enough toluene to allow effective stirring in CaH$_2$ overnight. The mixture was then filtered under argon through a celite bed with the aid of dry toluene. The toluene was then removed *in vacuo* resulting in the product as a colorless, opaque oil (8.3 g, 68%) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.58-1.75 (s, 3 H), 2.41-2.59 (q, 2 H), 4.22-4.35 (t, 1 H), 5.08-5.25 (m, 2 H), 5.71-5.96 (m, 1 H), 7.0-7.3 (m, 4 H); ^{13}C NMR ($CDCl_3$), 153.8, 149.0, 148.0, 133.3, 127.9, 120.5, 117.9, 67.7, 42.5, 33.0, 30.9. The IR spectrum (neat, KBr) showed absorptions at: 2975, 1770, 1640, 1250 cm^{-1}. Anal. Calcd. for $C_{25}H_{28}O_6$: C, 70.74; H, 6.64. Found: C, 70.80; H, 6.66.

Poly (5-decene) carbonate (20). In a drybox under a nitrogen atmosphere the molybdenum catalyst (0.012 g, 2.209 x 10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock followed by 15 (2.0 g, 8.8 x 10^{-3} moles). Rapid evolution of ethylene was evident and the reaction was allowed to stir until the reaction mixture thickened after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 hours. The reaction mixture which was then diluted with benzene (50 mL) and extracted with a sodium carbonate solution (3 x 50 mL) followed by water. The benzene fraction was then slowly added to a stirring solution of methanol precipitating the polymer as a white solid which was isolated via centrifugation. A vacuum was then applied to the polymer for a period of 24 hours resulting in the product as a white powder (1.6 g, 93%) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.25-1.51 (p, 2 H), 1.51-1.75 (p, 2 H), 1.88-2.10 (m, 2 H), 4.0-4.18 (t, 2 H), 5.28-5.42 (m, 1 H); ^{13}C NMR ($CDCl_3$), 155.4, 130.2, 129.6, 67.8, 32.0, 28.1, 25.7. The IR spectrum (film, KBr) showed absorptions at: 2900, 1745, 1260 cm^{-1}. Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 65.85; H, 9.11.

Poly (4-octene) carbonate (21). Preparation of 21 from the catalyst (0.0132 g, 2.52 x 10^{-5} moles) in the Schlenk tube was analogous to the procedure for 20 with 16 (2.0 g, 1.01 x 10^{-2} moles) to yield poly (4-octene) carbonate as an opaque, highly viscous oil (1,46 g, 85%) with the following spectral properties: ^1H NMR ($CDCl_3$), 1.60-1.82 (p, 2 H), 1.95-2.18 (m, 2 H), 4.0-4.2 (t, 2 H), 5.30-5.51 (m, 1 H); ^{13}C NMR ($CDCl_3$), 155.3, 129.8, 67.3, 28.6, 28.4,. The IR spectrum (film, KBr) showed absorptions at: 2950, 1750, 1360 cm^{-1}. Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.59; H, 8.29.

Poly (3-hexene) carbonate (22). Preparation of 22 from the catalyst (1.53 x 10^{-2} g, 2.94 x 10^{-5} moles) in the Schlenk tube was analogous to the procedure for 20 with 17 (2.0 g, 1.18 x 10^{-2} moles) to yield poly(3-hexene)carbonate as a white solid (1.57 g., 94%) with the following spectral properties: ^1H NMR ($CDCl_3$), 2.22-2.48 (m, 2 H), 4.0-4.2 (t, 2 H), 5.45-5.60 (m, 1 H); ^{13}C NMR ($CDCl_3$), 155.1, 128.1, 67.2, 31.9. The IR spectrum (film, KBr) showed absorptions at: 2960, 1745, 1260 cm^{-1}. Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 57.49; H, 7.23.

Attempted polymerization of 18. Catalyst (0.020 g, 3.84×10^{-7} moles) and 18 (1.0 g, 7.04×10^{-3} moles) were reacted in an analogous procedure for the synthesis of 20. Upon addition of the monomer to the catalyst there was no apparent evolution of ethylene and after 3 hours ^1H NMR revealed only unreacted starting material.

Poly(oxycarbonyloxy-1, 4-phenylene-iso-propylidene-1, 4-phenylene-oxycarbonyloxy-3-hexene) (23). Monomer 19 (2.0 g, 4.71×10^{-3} moles) and toluene (2 mL) were mixed together to allow efficient stirring of the monomer and then added to a Schlenk tube preloaded with catalyst (0.010 g, 1.92×10^{-5} moles). Rapid evolution of ethylene was evident and the reaction was allowed to stir until the reaction mixture thickened after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 hours. Benzene (50 mL) was then added to dilute the reaction mixture which was then extracted with a sodium carbonate solution (3 x 50 mL) followed by water. The benzene fraction was then slowly added to a stirring solution of methanol precipitating the polymer as a pale yellow solid which was isolated via centrifugation. A vacuum was then applied to the polymer for a period of 24 hours resulting in the product as a pale yellow solid (1.76 g, 94%) with the following spectral properties: ^1H NMR ($CDCl_3$), 1.55-1.80 (s, 3 H), 2.38-2.64 (m, 2 H), 4.16-4.38 (t, 2 H), 5.54-5.72 (m, 1 H); 7.0-7.38 (m, 4); ^{13}C NMR ($CDCl_3$), 153.7, 149.0, 148.0, 128.2, 127.9, 120.5, 67.9, 42.5, 31.9, 30.9. The IR spectrum (film, KBr) showed absorptions at: 2970, 1770, 1240 cm^{-1}. Anal. Calcd. for $C_{23}H_{24}O_6$: C, 69.68; H, 6.10. Found: C, 67.99; H, 6.21.

Dilute solution polymerization of 19. The polymerization was analogous to the procedure for the synthesis of 23, however, 19 (1.0 g, 2.36 x 10^{-3} moles) was dissolved in 10 mL of toluene before the addition of catalyst.

Poly[1-oxo-2,2,11,11-tetramethyl-6-undecenylene] (29). In a drybox equipped with nitrogen atmosphere 1a (0.020 g, 3.84 x 10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock followed by 6,6,8,8-tetramethyl-1,12-tridecene-7-one, 24 (2.0 g, 8.0 x 10^{-3} moles). Rapid evolution of ethylene was evident and the reaction was allowed to stir until the reaction mixture became too thick to stir after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 hours. The polymer was purified by first dissolving it in hexane followed by extraction with brine and sodium carbonate solutions. Removal of the hexanes resulted in the isolation of the polymer as an pale yellow solid (1.69, 95 %) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.05-1.28 (s, 18 H), 1.40-1.57 (m, 2 H), 1.8-2.0 (m, 2 H), 5.25-5.36 (m, 1 H); ^{13}C NMR ($CDCl_3$) 131.0, 129.0, 49.5, 41.5, 33.2, 26.2, 25.0.

Poly[(7-oxo-6,6,8,8-tetramethyl-1-undecenylene)-co-1-octenylene] (30). In a drybox equipped with nitrogen atmosphere 1a (0.020 g, 3.84 x 10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock followed by a premixed solution of 6,6,8,8-tetramethyl-1,12-tridecene-7-one, 25 (0.500 g, 2.00 x 10^{-3} moles) and 1, 9-decadiene (0.276 g, 2.00 x 10^{-3} moles). Rapid evolution of ethylene was evident and the reaction was allowed to stir until the reaction mixture became too thick to stir after which 2 mL of toluene was added. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional 8 hours. The polymer was purified by first dissolving it in hexane followed by extraction with brine and sodium carbonate solutions. Removal of the hexanes resulted in the isolation of the polymer as an pale yellow solid (1.2 g, 92 %) with the following spectral properties: ^{1}H NMR (CDCl3), 1.10-1.22 (s, 4 H), 1.22-1.40 (s, 2 H), 1.44-1.58 (m, 1 H), 1.84-2.06 (m, 2 H), 5.27-5.42 (m, 1 H); ^{13}C NMR (CDCl3) 125.4, 125.2, 125.0, 214.8, 48.5, 41.2, 33.1, 32.8, 29.8, 29.1, 27.8, 27.2, 26.1, 24.9.

Poly[(1-hexenylene-1,3-dimethyl-1,3-cyclododecylene-2-oxo-3-propylene)-co-1-octenylene] (31). Preparation of 31 from catalyst 1a (0.020 g, 3.84 x 10^{-5} moles) in the Schlenk tube was analogous to the procedure for 30 with a premixed solution of 2,12-(bis-5-pentene)-2,12-dimethyl-cyclododecyl-1-one, 26 (0.415 g, 1.20 x 10^{-3} moles) and 1, 9-decadiene (1.0 g, 7.2 x 10^{-3} moles) to yield 31 as a pale yellow solid (1.1 g, 95 %) with the following spectral properties: ^{1}H NMR (CDCl$_3$), 1.05-1.60 (br. s, 20 H), 1.75-2.10 (br. m, 8 H), 5.29-5.55 (m, 7 H); ^{13}C NMR (CDCl$_3$), 218.0, 139.1, 130.6, 130.3, 130.1, 129.8, 114.1, 53.3, 39.1, 33.8, 33.4, 32.6, 29.7, 29.6, 29.3, 29.2, 29.0, 28.9, 27.4, 27.2, 27.0, 24.6, 23.8, 23.6, 20.8. The IR spectrum (film, KBr) showed absorptions at: 2930, 2852, 2361, 2345, 1680, 1462, 1257, 968 cm^{-1}.

Poly[(1-propylene-1,3-cyclododecylene-2-oxo-3-propylene)-co-1-octenylene] (32). Preparation of 32 from catalyst 1a (1.53 x 10^{-2} g, 2.94 x 10^{-5} moles) in the Schlenk tube was analogous to the procedure for 30 with a premixed solution of 2,12-(bis-3-propene)-cyclododecyl-1-one, 27 (1.00 g, 3.81 x 10^{-3} moles) and 1,9-decadiene (3.17 g, 2.29 x 10^{-2} moles) to yield 32 as a pale yellow solid (3.13 g., 92 %) with the following spectral properties: ^{1}H NMR (CDCl$_3$), 1.10-1.45 (s, 13 H), 1.85-2.10 (m, 4 H), 5.28-5.45 (m, 1 H); ^{13}C NMR (CDCl$_3$), 217.0, 139.1, 130.3, 129.8, 114.1, 49.3, 33.8, 33.7, 32.6, 29.7, 29.6, 29.4, 29.2, 29.0, 28.9, 28.3, 27.2, 25.4, 24.6, 22.0.

Poly[(1-propylene-*trans*-1,3-dimethyl-1,3-cyclododecylene-2-oxo-3-methylene)-co-1-octenylene] (33). Preparation of 33 from catalyst 1a (1.53 x 10^{-2} g, 2.94 x 10^{-5} moles) in the Schlenk tube was analogous to the procedure for 30 with a premixed solution of trans-2,12-(bis-3-propene)-2,12-dimethyl-cyclododecyl-1-one, 28 (0.194 g, 6.68 x 10^{-4} moles) and 1, 9 decadiene (0.462 g, 3.34 x 10^{-3} moles) to yield 33 as a pale yellow solid (0.52 g., 95 %) with the following spectral properties: ^{1}H NMR (CDCl$_3$), 1.05-1.10 (s, 3

H), 1.12-1.48 (s, 14 H), 1.85-2.12 (s, 4 H), 5.29-5.45 (m, 1 H); ^{13}C NMR ($CDCl_3$), 131.0, 129.0, 39.6, 38.5, 32.4, 29.8, 28.8, 27.2, 26.2, 26.0, 22.5, 22.1, 20.1. The IR spectrum (film, KBr) showed absorptions at: 2928, 2856, 1709, 1465, 1440 cm^{-1}.

4,4,6,6-Tetramethyl-1,8-nonadiene-5-one (34). Diisopropylamine (8.86, 0.0876 moles) and THF (80 mL) were allowed to stir to dry ice/acetone temperatures under nitrogen in a 500 mL roundbottom flask via an addition funnel. N-BuLi (43.8 mL, 0.0876 moles) in a 2.0 molar solution of hexanes was added dropwise via the addition funnel maintaining the dry ice/acetone temperature after which the addition funnel was rinsed well with hexanes. The resulting lithium diisopropylamine (LDA) was then allowed to stir for an additional 15 minutes. The addition funnel was then charged with 2,4-dimethyl-3-pentanone (10.0, 0.0876 moles) in a small amount of THF which was then added slowly to the LDA solution. When the addition was complete the mixture was stirred overnight at room temperature. The solution was then cooled to 0°C after which 3-bromo-1-propene (10.6, 0.0876 moles) in a small amount of THF was added dropwise to the enolate solution (exothermic) after which the solution was allowed to stir at room temperature overnight. The reaction was then quenched by the addition of H_2O (100 mL) followed by diethyl ether (100 mL). The entire process was then repeated for the second alkylation. The mixure was then washed with water, 10% sodium thiosulfate, and finally brine. The aqueous fractions should be re-extracted since there seems to be significant product loss in the first set of washings after which the ether fractions were dried over magnesium sulfate. The product was purified yielding 34 as a colorless oil with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.18-1.25 (s, 6 H), 2.24-2.33 (d, 2 H), 4.92-5.06 (m, 2 H), 5.52-5.77 (m, 1 H); ^{13}C NMR ($CDCl_3$), 217.5, 135.0, 117.8, 49.1, 45.9, 25.8. The IR spectrum (film, KBr) showed absorptions at: 2978, 1684, 1639, 1472 cm^{-1}. Mass spectrum: (EI), m/e 194 (M^+).

2,2,7,7-Tetramethyl-4-cycloheptene-1-one (36). In a drybox equipped with nitrogen atmosphere 1a (0.020 g, 3.84×10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock followed by 4,4,6,6-tetramethyl-1,8-nonadiene-5-one, 34 (2.0 g, 0.0103 moles). Rapid evolution of ethylene was evident and the reaction was allowed to stir for one hour. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional two hours. The mixture was then vacuum transfer resulting in the isolation of the cyclized product as colorless oil (1.7 g, 99 %) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.08-1.13 (s, 6 H), 2.23-2.28 (d, 2 H), 5.68-5.75 (m, 1 H); ^{13}C NMR ($CDCl_3$) 218.6, 128.1, 48.9, 39.0, 27.5. Anal. Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.34; H, 10.87. Mass spectrum: (EI), m/e 166 (M^+).

1,11 Dimethyl-bicyclo-[9.4.1]-13-hexadecene-16-one (37). In a drybox equipped with nitrogen atmosphere 1a (0.020 g, 3.84×10^{-5} moles) was weighed into a Schlenk tube equipped with a stopcock followed by cis-2,12-(bis-3-propene)-2,12-dimethyl-cyclododecyl-1-one, 35 (1.0 g, 3.4 x 10^{-3} moles). Rapid evolution of ethylene was evident and the reaction was allowed to stir for one hour. The reaction vessel was then closed off to the atmosphere, removed from the drybox, and attached to a vacuum line where a static vacuum was applied and the reaction mixture allowed to stir for an additional two hours. The cyclized compound was purified by first dissolving it in hexane followed by extraction with brine and sodium carbonate solutions. Removal of the hexanes resulted in the isolation of the product as a colorless oil (0.89, 99 %) with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.00-1.12 (s, 6 H), 1.15-1.50 (m, 18 H), 1.60-1.81 (m, 1 H), 2.04-2.10 (d, 1 H), 2.10-2.18 (d, 1 H), 2.42-2.48 (d, 1 H), 2.50-2.56 (d, 1 H), 5.86-5.98 (t, 1 H); ^{13} C NMR ($CDCl_3$) 216.8, 130.4, 94.0, 54.2, 39.4, 38.4, 26.3, 26.1, 22.9, 20.3. The IR spectrum (neat, KBr) showed absorptions at: 3340, 2900, 1683 cm^{-1}. Mass spectrum: (EI), m/e 262 (M^+).

1-(2,2-Dimethyl-propane-1-one)-1-methyl-3-cyclopentene (47). In a drybox equipped with nitrogen atmosphere 4-(3-propane)-2,2,4-trimethyl-6-heptene-3-one, 42 (0.50 g, 2.75 x 10^{-3} moles), and catalyst 1a (0.01 g, 1.9 x 10^{-5} moles) were mixed togather and allowed to stir for three hours after which ^{1}H NMR revealed both starting material and cyclized product, 47 (60 % by ^{1}H NMR), with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.22-1.23 (s, 9 H), 1.25-1.26 (s, 3 H), 2.10-2.27 (m, 2 H), 2.85-3.10 (m, 2 H), 5.54-5.61 (m, 2 H). Mass spectrum: (EI), m/e 166 (M^+).

1-(2-Methyl-2-phenyl-propane-1-one)-1-methyl-3-cyclopentene (48). In a drybox equipped with nitrogen atmosphere 2,4-dimethyl-2-phenyl-4-(3-propene)-6-heptene-3-one, 43 (0.30 g, 1.2 x 10^{-3} moles), and catalyst 1a (0.01 g, 1.9 x 10^{-5} moles) were mixed togather and allowed to stir for three hours after which ^{1}H NMR revealed both starting material and cyclized product, 48 (95 % by ^{1}H NMR), with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.35-1.45 (s, 3 H), 2.30-2.50 (m, 2 H), 3.08-3.26 (m, 2 H), 5.70-5.81 (s, 2 H), 7.35-7.58 (m, 3 H), 7.80-7.92 (m, 2 H). Mass spectrum: (EI), m/e 216 (M^+).

1,1-Dimethylester-3-cyclopentene (49). In a drybox equipped with nitrogen atmosphere bis-(3-propenyl)-methyl-malonate, 44 (0.10 g, 1.9 x 10^{-5}, and catalyst 1a (0.01 g, 1.9 x 10^{-5} moles) were mixed togather and allowed to stir for three hours after which ^{1}H NMR revealed only linear oligomers with the following spectral properties: ^{1}H NMR (d_6-benzene), 3.10-3.28 (s, 3 H), 3.30-3.42 (s, 2 H), 5.37-5.49 (m, 1 H).

1-(2,2-Dimethyl-propane-1-one)-1-methyl-3-cyclohexene (50). In a drybox equipped with nitrogen atmosphere 4-(3-propenyl)-2, 2, 4-trimethyl-7-octene-3-one, 45 (0.40 g, 2.04 x 10^{-3} moles), and catalyst 1a (0.010 g, 1.9 x 10^{-5} moles) were mixed togather and allowed to stir for three hours after which ^{1}H NMR revealed both starting material and cyclized product, 50 (60 % by ^{1}H NMR), with the following spectral properties: ^{1}H NMR ($CDCl_3$), 1.00-1.07 (d, 2

H), 1.10-1.18 (s, 3 H), 1.18-1.30 (s, 9 H), 1.90-2.10 (m, 4 H), 5.58-5.62 (t, 2 H). Mass spectrum: (EI), m/e 168 (M^+).

1-(2,2-Dimethyl-propane-1-one)-1-methyl-4-cycloheptane(51). In a drybox equipped with nitrogen atmosphere 5-(2,2-dimethyl-propane-1-one)-1, 8-nonadiene, 46 (0.50 g, 2.25 x 10^{-5} moles), and catalyst 1a (0.010 g, 1.9 x 10^{-5} moles) were mixed togather and allowed to stir for three hours after which ^1H NMR revealed both starting material and cyclized product, 51 (20 % by ^1H NMR), with the following spectral properties: ^1H NMR ($CDCl_3$), 1.08-1.17 (s, 3 H), 1.18-1.24 (s, 9 H), 1.70-2.00 (m, 8 H), 5.58-5.62 (t, 2 H). Mass spectrum: (EI), m/e 194 (M^+).

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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